DTIC FILE COPY

AL-TR-90-047

AD:

(2)

Inverse Gas Chromatography

Final Report
for the period
February 1987 to
January 1990

DTIC
ELECTE
OCT 17 1990
S B D

AD-A227 677

September 1990

Author:
R.J. Laub

San Diego State University
Department of Chemistry
San Diego CA 92182

F04611-87-K-0006

Approved for Public Release

Distribution is unlimited. The AL Technical Services Office has reviewed this report, and it is releasable to the National Technical Information Service, where it will be available to the general public, including foreign nationals.

Prepared for the: **Astronautics Laboratory (AFSC)**
Air Force Space Technology Center
Space Systems Division
Air Force Systems Command
Edwards AFB CA 93523-5000

90 10 17 006

NOTICE

When U. S. Government drawings, specifications, or other data are used for any purpose other than a definitely related Government procurement operation, the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise, or in any way licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may be related thereto.

FOREWORD

This final report was submitted by San Diego State University, San Diego CA on completion of contract F04611-87-K-0006 with the Astronautics Laboratory (AFSC), Edwards AFB CA. AL Project Manager is Roy Wurzbach.

This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the DD Form 1473.

Roy A. Wurzbach

ROY A. WURZBACH
Project Manager

WILLIAM C. HURLEY, MAJOR, USAF
Chief, Chemical Sciences Branch

FOR THE DIRECTOR

Robert C Corley

ROBERT C. CORLEY
Director, Astronautical Sciences Division

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S) AL-TR-90-047
6a. NAME OF PERFORMING ORGANIZATION San Diego State University 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Astronautics Laboratory (AFSC)
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry San Diego, CA 92182	7b. ADDRESS (City, State, and ZIP Code) AL/LSSP Edwards AFB CA 93523-5000
8a. NAME OF FUNDING/SPONSORING ORGANIZATION 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F04611-87-K-0006
8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
62302F	5730	006C	354517

11. TITLE (Include Security Classification)
Inverse Gas Chromatography (U)

12. PERSONAL AUTHOR(S)
Laub, Richard J.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final Technical Report	FROM 87/02 TO 90/01	9009	151

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	
21	09	2	Hydroxy-Terminated Polybutadiene, R-45M, Prepolymer Characterization, Chromatography
19	07		

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Some fundamental aspects of the physicochemical characterization of propellant prepolymers were explored for the purpose of developing and optimizing analytical procedures for molecular weight, degree of branching, and functionality distributions. Inverse gas and gel permeation chromatography, and Fourier-transform infrared spectroscopy, were employed with bulk and fractionated R-45M. The methodologies and techniques of analysis ultimately developed make use only of readily-available equipment, and are applicable to characterization and routine quality control of virtually any prepolymer system. They can therefore be implemented in any vendor or government laboratory.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED
22a. NAME OF RESPONSIBLE INDIVIDUAL Roy A. Wurzbach	22b. TELEPHONE (Include Area Code) (805) 275-5414 22c. OFFICE SYMBOL LSSP

DD Form 1473, JUN 86 Previous editions are obsolete. SECURITY CLASSIFICATION OF THIS PAGE

TABLE OF CONTENTS

Accession For
NTIS GRA&I ☑
DTIC TAB ☐
Unannounced ☐
Justification
By
Distribution/
Availability Codes
Dist | Avail and/or Special
A-1

DTIC COPY INSPECTED

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Polymeric binder materials have been used for some time as composite propellants in a number of Defense systems (1-3). These include: polyneopentyl glycol azelate (NPGA) in HAWK; hydroxy-terminated polybutadiene (HTPB) in VIPER, PATRIOT, MET ROCKET, GSRS, PERSHING, and HELLFIRE; polybutadiene acrylic acid (PBAA) in PERSHING and SPARTAN; and polyethylene glycol (PEG), polyethylene glycol adipate (PEGA), and polycaprolactone (PCL) in composite smokeless propellants.

However, the polydisperse nature of these binders gives rise to significant differences in the various combustion properties of the respective propellant, hence the engine itself. Further compounding the problem is that the analytical procedures currently employed for characterization of the respective prepolymers are difficult and time-consuming. Moreover, there is considerable disagreement at the present time regarding interpretation of the results of such analyses even when performed in good faith, and correlation of the results with the properties (e.g., curing) of the resultant polymer (4-8).

Contract F04611-84-K-0016 was therefore let by the Air Force Astronautics Laboratory to Prof. R. J. Laub to explore and to clarify the situation regarding the analysis of propellant prepolymers; and to develop and optimize strategies pertaining to speciation according to molecular weight, to degree of branching, and to functionality distribution. The methods employed in that work centered largely upon liquid chromatography, gel permeation chromatography, density, viscosity, vapor-phase osmometry, differential scanning calorimetry, infrared and nuclear magnetic resonance spectroscopy, and mass spectrometry.

It was also found during the course of the work that the technique known as "inverse" gas chromatography (IGC) offered an additional and very powerful supplemental tool for the characterization of R-45M. Moreover, the method appeared to be simpler, faster, more accurate, and provide a much higher information content, than any combination of conventional techniques currently employed for these purposes.

Briefly, IGC makes use of the retention behavior of probe-solutes to examine the properties of the stationary phase (here, R-45M). For example, discontinuities in van't Hoff plots of log(retention) against inverse temperature can be used to determine polymer glass transitions, liquid-crystalline phase behavior, and so forth. However, the technique can also be used to assess the stationary-phase molecular weight and hydroxyl content; and, potentially, the type and extent of chain branching as well.

Some very promising results were then obtained in preliminary work. As a result, and since virtually nothing was known about the utility of IGC for species such as hydroxy-terminated polybutadiene, the current Contract, F04611-87-K-0006, was let for exploratory study and further assessment of the inverse gas-chromatographic technique as a method for characterizing R-45M. In addition, it was intended that the fundamental analytical developments and resultant practical methodologies and techniques arising from the work also be made applicable to analysis and routine quality control of virtually any prepolymer system, particularly those that are not readily amenable to characterization by the above-mentioned conventional means.

THEORY OF INVERSE GAS CHROMATOGRAPHY

Interest in the polymer uptake of simple to complex compounds dates back to well before the time of Raoult, and has included such diverse phenomena as the aqueous swelling of cellulose and the fast-dyeing of fibers. In this Century, the experimental study of solute/polymer interactions has for the most part centered upon activity coefficient data, and their interpretation in terms of theories such as those associated with

Hildebrand, Scatchard, Flory, Prigogine, Patterson, and others. However, while these efforts have certainly been attended with some success, it can hardly be claimed that any high degree of quantitative reconciliation has been achieved for other than simple hydrocarbon systems. Nor is the matter a trivial one, since activity coefficients and the associated thermodynamic properties of solution account for very many physicochemical phenomena of both fundamental as well as applied interest in many branches of the physical sciences.

Closely allied with the above, inverse gas chromatography has been used extensively for the study of solute-polymer interactions, including phase transitions: this or that material is employed as a stationary phase, and discontinuities in van't Hoff plots of log (probe-solute relative retentions) (usually n-alkanes) are used to determine e.g. the degree of crystallinity, glass transitions, and so forth. Solute/polymer activity and partition coefficient data are also readily derived from the technique, and have been employed inter alia to investigate polymer swelling and solute/polymer surface adsorption.

The GC method of characterizing polymeric solvents derives initially from the relation (9):

$$K_R^o = RT/{}^x\gamma_A^\infty f_A^o \bar{V}_S \qquad (1)$$

where K_R^o is the fully-corrected solute liquid-gas partition coefficient, ${}^x\gamma_A^\infty$ is the solute mole-fraction based Raoult's-law activity coefficient, f_A^o is its fugacity (approximately equal to its vapor pressure) at the column temperature T, and $\bar{V}_S$ is the molar volume of the solvent (stationary phase). Partition coefficients are measured directly in the GC technique, from which ${}^x\gamma_A^\infty$ are calculated and from which the excess thermodynamic properties can then be derived. van't Hoff plots either of ln K_R^o or of ln ${}^x\gamma_A^\infty$ against T^{-1} also yield information regarding phase transitions.

In the instances of polymeric solvents, the solute specific retention volume V_g^o (units of $cm^3\ g^{-1}$) is utilized:

$$V_g^o = K_R^o(273/r_S T = 273R/{}^w\gamma_A^\infty p_A^o M_A \qquad (2)$$

where r_S is the density of the stationary phase and ${}^w\gamma_A^\infty$ is the weight-fraction based activity coefficient of the solute of molecular weight M_A; where mole- and weight-fraction based activity coefficients are related by:

$${}^w\gamma_A^\infty = {}^x\gamma_A^\infty M_S/M_A \qquad (3)$$

The inverse gas chromatographic technique thus can be used to assess physicochemical properties (viscosity, functionality, molecular weight, etc.) of the liquid phase via measurement of the specific retention volumes and/or activity coefficients of probe-solutes. That is, the microstructure of this or that material can be determined simply by fabricating a GC packing from it and then measuring the retentions of appropriate probe-solutes. Moreover, high-precision gas chromatographic instrumentation (10) is capable of levels of reproducibility of ± 1%.

For example, according to eqn. 1, partition coefficients vary inversely as the stationary-liquid molecular weight and so, the retentions of n-alkanes offer a measure of M_S irrespective of the nature of the prepolymer. Also, alcohol and ketone solutes are presumably sensitive to the hydroxyl content of species such as R-45M and so, would be the appropriate probe-solutes for gauging this property of this prepolymer. In addition, simulated aging can be carried out by passing air of a given humidity through the column at some appropriate temperature and then rechromatographing the probe-solutes; where differences in the retentions measured before and after aging reflect the kinds and magnitudes of changes that have taken place.

CONTRACT OVERVIEW. PHASE I: PRELIMINARY ASSESSMENT; MOLECULAR-WEIGHT DISTRIBUTION

The initial Phase of this Contract was designed to confirm, first, that IGC retentions indeed correlate at least with molecular weight; and, secondly, to establish which solutes exhibit the greatest sensitivity to molecular-weight differences in lots of R-45M. It was then intended that nomographs of solute retentions (of whatever form) against some function of the stationary-phase molecular weight be constructed and tested.

Task 1. Preliminary Assessment of Probe-Solute Retentions with Lots of R-45M

In carrying out the preliminary studies, the specific retention volumes V_g^o and activity coefficients γ_A^∞ of a variety of probe solutes were measured with several purportedly well-characterized batches of R-45M by high-precision gas-liquid chromatography (GLC) at from 30° to 80°C at intervals of 10°. Aliphatic, heterofunctional aliphatic, alicyclic, heterocyclic, and aromatic hydrocarbon solutes were considered (ca. 30 in all). Replicate runs with several batches of R-45M were also performed. Liquid loadings were ca. 5% on Chromosorb G (AW; DMCS-treated); one batch was repeated with 10% w/w liquid loading to check for gas-liquid interfacial effects. From these data, the Gibbs free energy $\Delta\bar{G}_S$, enthalpy $\Delta\bar{H}_S$, and entropy $\Delta\bar{S}_S$ of solution were calculated from the specific retention volumes; and, also, from the activity coefficients, the excess free energy G^e, enthalpy H^e, entropy S^e, heat capacity C_p^e, and Flory-Huggins interaction parameter X. The probe-solutes whose retentions appeared to be a function of prepolymer molecular weight were then identified.

Task 2. Average Molecular Weight

Narrow molecular-weight fractions of two batches of R-45M were cut by solvent extraction. The molecular weights of each were characterized by suitable means. All probe-solutes were run with each fraction. The solutes whose retentions correlated with prepolymer molecular weight were identified. Functions capable of reduction to nomograph form that directly relate probe-solute retentions with prepolymer molecular weight were then formulated. Several polybutadiene prepolymers, characterized by GPC, were employed as stationary phases for further confirmation of the choice of appropriate probe-solutes and the retention/molecular-weight nomographs (i.e., materials similar to R-45M except for hydroxyl content).

PHASE II: HYDROXYL CONTENT

The second Phase of the Contract was designed to investigate the assessment of hydroxyl content of R-45M by inverse gas chromatography. The OH contents of several lots of R-45M were to be measured first by the classical technique of FT-IR. Probe-solutes whose retentions correlated with OH content were then to be identified.

Task 1. Wet-Chemical/Instrumental Determination of Absolute Hydroxyl Content

In the initial stages of this Phase, several grams of narrow molecular-weight fractions of three purportedly well-characterized batches of R-45M used in Phase I, Task 1, were cut by the solvent-extraction method. The molecular-weight ranges of each fraction of each prepolymer were measured by GPC. The hydroxyl contents of the fractions were also measured by FT-IR.

Task 2. GLC Determination of Hydroxyl Content

Several of the prepolymers were next used as GLC stationary phases. The complete bank of probe-solutes was employed at 30-80°C and the retention information (V_g^o, etc.) described in Phase I, Task 1 was derived. It was found that several of the probe-solutes exhibited retentions that correlated with the hydroxyl content. Nomographs that directly relate probe-solute retentions with prepolymer hydroxyl content were formulated.

Task 3. Hydroxyl Distribution

At least one diketone solute was included with the bank of probe-solutes. It was intended to attempt to correlate its retentions with hydroxyl distribution in terms of elution times that are in excess of those for the previously-identified hydroxyl-content probe-solutes. That is, the retentions of the diketone would be expected to be identical to a monoketone of the same carbon number if the hydroxyl distribution were uniform. However, the former would exhibit longer retentions than the latter if the prepolymer contained closely-spaced hydroxyl groups with which both carbonyls of the diketone could interact simultaneously. The results were ambiguous.

PHASE III: CHARACTERIZATION

The third Phase of the Contract was designed to demonstrate the characterization of three or four selected lots of R-45M by inverse gas chromatography. It was intended in particular to determine if differences in the inverse GC retentions could be correlated with changes in the physicochemical properties of the polymers. Provided they were available, it was also hoped that the results could be correlated with polymer viscoelastic properties provided by AL.

Task 1. Inverse GC of Selected Lots of R-45M

Four lots of R-45M were characterized by IGC in terms of molecular weight and hydroxyl content in this portion of the work. Three of the materials were provided by AL (lots "40", "42B", and "V004"; see later), while the fourth, R20LM, was received from Sartomer. The latter material was said to be a "standard" batch of prepolymer that was similar to ARCO X-20LM.

Task 2. Chain Branching

Chain branching effects on the GC retentions were looked for; none were evident. This result correlated with that obtained for chain branching by classical techniques (Drott analysis, etc.) in the previous Contract effort, viz., that chain branching in these samples cannot be detected by the methods employed.

EXPERIMENTAL SECTION

Apparatus and Equipment

The high-precision gas chromatograph employed in this work was equivalent to the system described and discussed elsewhere (10,11). Briefly, the GC consisted of a water-bath column thermostat (Neslabs Endocal RTE-8 capable of ± 0.05° precision, as measured to ± 0.02° with a Hewlett-Packard 2802A digital read-out platinum resistance system), a Hamilton glass-lined injection port, a Brooks dual-channel flow controller, a

Gow-Mac thermal conductivity detector, and a Houston Instruments stripchart recorder. The instrument was also fitted with a soap-bubble flowmeter and U.S. Gauge gauges for measurement of the column sample and reference inlet pressures. Retention times were measured to ± 0.01 sec with a Siliconix ET 200 electronic stopwatch. The analytical GC was a conventional Varian Model 14 (FID detection).

The FT-IR was a Mattson Alpha-Centauri system, equipped with a standard solutions cell (sodium chloride windows).

The gel-permeation chromatograph was a Varian Model 8500, equipped with a Rheodyne injection valve and a Knauer differential refractometer. The solvent was stabilized (BHT) tetrahydrofuran (THF) throughout. The GPC column was from PL Laboratories, 30 cm x 9 mm i.d., and was 1000 Angstroms in porosity.

Materials and Supplies

Prepolymers. Samples of R-45M, designated as Poly bd X-10LM, X-14LM, X-20LM, X-25LM, and X-120HM, were obtained from ARCO Chemical Co., Newtown Square, Pa. The materials have been described elsewhere by Hinney, Babiec, Jr., and Murphy (12), and by Arnold, Baghdadchi, Hinney, and Meyers (13), and are summarized below in Table 1. Samples of R-45M designated at lots 40, 42B, and V004 were received from Thiokol via AL. Additional R-45M lots are described later. One sample of R-45M, R20LM, was obtained from Sartomer, and was claimed to be nearly identical to ARCO X-20LM. The polybutadiene standards, also obtained from AL, were originally from Goodyear. All other chemicals and reagents were from Aldrich or were supplied by AL.

TABLE 1. Properties of Indicated Bulk Lots of ARCO R-45M (12,13)

Designation	n/cP (25°C)	M_n/Da	M_n/M_w	OH/meq g^{-1}
10LM	988	1 040	1.7	1.73
14LM	1 450	1 420	1.5	1.40
20LM	1 868	1 350	1.4	1.40
25LM	2 610	1 630	1.2	1.18
120HM	11 462	3 335	-	0.59

Probe-Solutes. Roughly 30 solutes were employed throughout this work. They were chosen so as to provide data representative of the behavior of straight, branched, alicyclic, heterocyclic, aromatic, and halohydrocarbons.

Physical Properties. The molecular weights and critical properties of the probe-solutes are listed in Table 2 (14-16). The latter data were required for calculation of the fugacity correction to the solute activity coefficients (17).

Antoine Constants and Vapor Pressures. In order to calculate solute activity coefficients it is necessary to know their vapor pressures at the temperature(s) of interest. The most expeditious means of reporting such data over a range of temperatures (t in °C) is with what is known as the Antoine equation:

$$\log p_A^o = A - [B/(t/°C + C)] \qquad (4)$$

The constants A, B, and C are then known as the Antoine constants, and are temperature-independent. Solute vapor pressures p_A^o can thereby be calculated at any temperature of interest over which the constants are valid.

The Antoine constants (16,18-20) for the probe-solutes employed in this work are provided in Table 3 below; while the resultant calculated vapor pressures at 30-80°C are then presented in Table 4 following.

TABLE 2. Molecular Weights M/Da, and Critical Temperatures T^c/K and Volumes $V^c/cm^3\ mol^{-1}$ for Indicated Probe-Solutes (14-16)

Probe Solute	M/Da	T^c/K	$V^c/cm^3\ mol^{-1}$
n-Pentane	72.146	469.77	311.021
n-Hexane	86.172	507.85	368.041
n-Heptane	100.198	540.16	426.042
n-Octane	114.224	569.35	486.023
3-Methylpentane	86.1727	504.35	367.007
2,3-Dimethylpentane	100.198	537.75	405.000
3-Methylhexane	100.198	535.55	418.026
3-Methylheptane	114.224	565.15	478.027
1-Hexene	84.156	501.15	365.405
1-Heptene	98.182	535.15	416.979
1-Octene	112.208	565.15	468.244
Benzene	78.108	562.60	260.334
Toluene	92.134	593.95	319.981
Ethylbenzene	106.160	619.55	366.040
o-Xylene	106.160	632.15	380.053
p-Xylene	106.160	618.15	369.437
Cyclohexane	84.156	554.15	309.610
Methylcyclohexane	98.182	572.15	344.521
Tetrahydrofuran	72.108	541.15	223.967
Thiophene	84.138	570.15	249.890
Acetone	58.081	508.15	208.975
Methyl Ethyl Ketone	72.108	536.75	267.016
Methyl Propyl Ketone	86.135	561.05	301.042
Methyl Butyl Ketone	100.162	587.05	-
Acetylacetone	128.173	-	-
Methylene Chloride	84.940	525.15	-
Chloroform	119.389	536.35	239.005
1-Chloropentane	106.595	-	-
n-Butyronitrile	69.107	582.25	-
n-Valeronitrile	83.134	-	-

TABLE 3. Antoine Constants A, B, and C (16,18-20) (Cf. Eqn. 4) for Indicated Probe-Solutes

Probe Solute	A	B	C
n-Pentane	6.85221	1064.63	232.2
n-Hexane	6.87776	1171.53	224.366
n-Heptane	6.90240	1268.115	216.90
n-Octane	6.92377	1355.126	209.517
3-Methylpentane	6.84887	1152.368	227.129
2,3-Dimethylpentane	6.85382	1238.017	221.823
3-Methylhexane	6.86764	1240.196	219.223
3-Methylheptane	6.89944	1331.53	212.414
1-Hexene	6.86572	1152.971	226.0
1-Heptene	6.90069	1257.505	219.18
1-Octene	6.93263	1353.5	212.764
Benzene	6.90565	1211.033	220.79
Toluene	6.95334	1343.943	219.377
Ethylbenzene	6.95719	1424.255	213.206
o-Xylene	6.99891	1474.679	213.686
p-Xylene	6.99052	1453.43	215.307
Cyclohexane	6.84498	1203.526	222.863
Methylcyclohexane	6.82689	1272.864	221.630
Tetrahydrofuran	6.99515	1202.29	226.254
Thiophene	6.95926	1246.038	221.354
Acetone	7.129877	1216.689	230.275
Methyl Ethyl Ketone	7.059537	1259.223	221.758
Methyl Propyl Ketone	7.014347	1309.592	214.561
Methyl Butyl Ketone	7.037397	1401.738	209.646
Acetylacetone	6.86495	1377.34	208.35
Methylene Chloride	7.07138	1134.6	231.0
Chloroform	6.90328	1163.0	227.0
1-Chloropentane	6.96617	1332.890	218.50
n-Butyronitrile	7.70502	1825.767	260.971
n-Valeronitrile	7.10487	1519.367	218.435

TABLE 4. Probe-Solute Vapor Pressures p_A^o/torr at 30-80°C

	p_A^o/torr					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	619.4	873.2	1201.	1617.	2135.	2768.
n-Hexane	187.2	279.6	405.5	573.0	790.9	1069.
n-Heptane	58.39	92.52	141.6	210.3	303.7	427.8
n-Octane	18.46	31.12	50.38	78.70	119.1	175.1
3-Methylpentane	232.9	342.7	490.4	684.5	934.2	1250.
2,3-Dimethyl-pentane	86.61	133.5	199.2	289.0	408.8	565.0
Methylhexane	77.85	121.1	182.4	266.6	379.8	528.2
3-Methylheptane	25.51	42.10	66.88	102.7	153.0	221.7
1-Hexene	230.0	339.7	487.7	682.7	934.2	1252.
1-Heptene	71.47	111.9	169.5	249.1	356.6	498.4
1-Octene	22.76	37.82	60.47	93.40	139.9	203.9
Benzene	119.4	182.9	217.4	391.6	551.0	757.9
Toluene	36.67	59.17	92.14	139.0	203.8	291.3
Ethylbenzene	12.62	21.49	35.15	55.46	84.74	125.8
o-Xylene	8.858	15.34	25.49	40.80	63.19	94.98
p-Xylene	11.63	19.85	32.54	51.45	78.78	117.2
Cyclohexane	121.7	184.7	271.8	389.3	543.9	743.4
Methylcyclo-hexane	58.65	91.54	138.3	202.8	289.8	404.4
Tetrahydrofuran	201.0	301.7	439.5	623.8	864.6	1173.
Thiophene	100.5	155.5	233.0	339.4	481.6	667.7
Acetone	285.3	424.9	615.0	867.8	1197.	1617.
Methyl Ethyl Ketone	114.3	177.4	266.7	389.4	554.1	770.3
Methyl Propyl Ketone	45.64	74.09	115.9	175.6	258.3	370.1
Methyl Butyl Ketone	15.43	26.47	43.55	69.05	105.9	157.8
Acetylacetone	12.20	20.85	34.19	54.02	82.59	122.6
Methylene Chloride	530.0	766.8	1081.	1487.	2004.	2650.
Chloroform	238.8	352.8	506.7	709.6	971.6	1303.
1-Chloropentane	40.00	64.55	100.5	151.4	221.9	316.9
n-Butyronitrile	26.92	43.51	68.19	103.9	154.3	224.0
n-Valeronitrile	9.753	16.82	27.85	44.47	68.75	103.2

Procedures

Packed GC columns were prepared by deposition via rotary evaporation of the stationary phase from methylene chloride solution onto the solid support, here, 60/80-mesh Chromosorb G (AW/DMCS-treated). Packings were then displaced by suction into 3- (analytical) or 6-mm i.d. stainless-steel or nickel columns of approximately 1-2 m in length, and were conditioned under helium flow overnight at 80°C. Data acquisition and reduction were then carried out in the usual way (9,10).

Solvent extraction was carried out by fractional solution with combinations of isopropyl alcohol (IPA) and benzene in a water-jacketed separatory funnel at 30°C, as described by Laub (11). Nine fractions were obtained, corresponding to two extractions each with pure IPA (1A, 1B), 10% v/v benzene + IPA (2A, 2B), 20% benzene + IPA (3A, 3B), 30% benzene + IPA (4A, 4B), and 40% benzene + IPA (5A).

FT-IR data reduction was as described previously by Emanuel and Dee (21) and by Laub (11). Gel-permeation chromatography was carried out as described elsewhere by Laub (11).

RESULTS AND DISCUSSION

Phase I, Task 1. Preliminary Assessment of Probe-Solute Retentions with Lots of R-45M

Prior to initiation of this Contract, virtually nothing was known about the activity and partition coefficients of probe-solutes with neat or blended-polymer systems of Defense-related interest (for example, hydroxy-terminated polybutadiene, or mixtures of this with polybutadiene acrylic acid; polyethylene glycol + polyethylene glycol adipate; etc.). Furthermore, yet to be explored in any detail was the variation of activity coefficients of probe-solutes such as alcohols, ketones, olefins, and aromatic compounds with various separate (polydisperse) prepolymers, let alone with copolymer systems; nor of the influence of prepolymer molecular-weight distribution and functionality. Accordingly, and because of the attendant advantages of simplicity, precision, ease, and accuracy of the inverse gas-chromatographic technique, the IGC method was evaluated in preliminary work from the standpoint of its potential as a supplemental tool for the characterization of Defense-related prepolymer materials. In the course of doing so, the specific retention volumes of a bank of 23 solutes, comprised of normal- and branched aliphatic, aromatic, alicyclic, heterocyclic, and heterofunctional hydrocarbons, were determined over the temperature-span 30-80°C with three batches of R-45M and two lots of polybutadienes (PBD).

Preliminary Evaluation of the Inverse GC Technique. Several aspects of the use of PBD as well as R-45M as GC solvents required preliminary evaluation, such as reproducibility of the retentions, temperature stability of the stationary phase, and so forth. Each is considered in turn in what follows below.

Reproducibility of the GC Technique. Despite the very many studies over the years that have confirmed the reproducibility of the GC technique in general (9-11), an investigation was nevertheless carried out of the precision with which probe-solute specific retention volumes with R-45M could be measured with the instrumentation to hand in this Laboratory. Also, it was not known in advance whether this prepolymer was suitable for use as a stationary phase, that is, whether its volatility was sufficiently low (ca. 0.01 torr) at upwards of 100°C; and whether the material was stable at least over the duration of the use of the columns (ca. 3 days each).

It was found, first, that R-45M (as well as PBD of 1000 and 2500 Da; see later) was ideally suited as a stationary phase insofar as no column bleed was observed at the maximum temperature (90°C) of the system thermostat and at maximum sensitivity of

the thermal conductivity detector. In addition, repeated cycling of the temperature, coupled with reinjection of several of the solutes, demonstrated that the properties of the stationary packings remained invariant over the course of individual experiments. Accordingly, the fully-corrected specific retention volumes $V_g^o/cm^3\ g^{-1}$ for all probe-solutes (minimum of three replicate injections of each) were determined with three columns of the same lot of R-45M at 70-90°C (prepolymer supplied by AL; 60/80- or 120/140-mesh AW/DMCS-treated Chromosorb G support). The experimental data are provided below in Table 5; where column A corresponds to a 9% w/w loading of liquid phase while (replicate) columns B and C were comprised of ca. 5% loadings. The average discrepancy between the columns of roughly equal stationary-phase content was observed to be considerably less than 1%, while the heavier-loaded column, A, showed discrepancies with B,C on average of about 1%.

Lot-to-Lot Variations of R-45M. Shown next in Table 6 are the averaged retentions of the probe-solutes obtained with Lot A (Table 5; 5% loaded columns), together with the specific retention volumes yielded by two Lots, B and C, of R-45M supplied by United Technologies. Recalling that the level of experimental error is on the order of 1%, there are immediately apparent several experimentally-significant shifts in the retentions from one batch of this material to another.

Considering first the n-alkanes, whose retentions are presumably a function only of the solvent molecular weight, it was found that n-octane was retained the longest with Lot C at 70°C and exhibited the shortest retention with Lot A. However, this order was exactly reversed on passing to 80° and 90°C, at which temperatures Lot A yielded the largest retention for this hydrocarbon. The retentions for all branched alkanes except 3-methylheptane fell, as above, to within experimental error. However, this was not so for the latter solute which, as with n-octane, was retained longest by Lot C at 70°C. The same trend was observed upon consideration of the olefins and, in particular, 1-octene.

The retentions of the alicyclic and aromatic hydrocarbons were quite remarkable. All were retained to about the same extent at 70°C by Lots A and B, yet eluted much later from Lot C. However, the converse was true at 80° and 90°C: here, the probe-solutes were retained longest by Lot A and least by Lot B, with the specific retention volumes observed for Lot C falling in between. The behavior is reminiscent of a second-order phase transition, although what form this might take with R-45M (and/or whether it might be an artifact of the GC technique) is at present open to question. The probe-solutes THF and thiophene were of little help in speciating the effect, as their retentions were indistinctly different from one lot to another at all three temperatures.

The probe-solute ketones were expected at the outset to show the greatest differences in retentions on passing from one batch of R-45M to the next, since they are presumably retained almost entirely as a result of hydrogen bonding. Indeed, the specific retention volumes of methyl propyl ketone and methyl butyl ketone were found to be nearly an order of magnitude larger than those of the corresponding n-alkanes, i.e., n-pentane and n-hexane; nor can the differences be explained on the basis of the vapor pressures of these solutes. Even so, each ketone was retained by each lot of R-45M to about the same extent at a given temperature, which indicated that a lower column temperature was required in order to detect differences in hydroxyl content. However, the same was not so for acetylacetone (2,4-pentanedione): the retentions of this solute were markedly greater with Lot A than with B or C at all three temperatures considered in this work. There was also an inversion in the retention order of acetylacetone and methyl butyl ketone on passing from Lot A to Lot B at 70°C.

TABLE 5. Test of Reproducibility of the Inverse GC Technique: Fully-Corrected Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ for the Indicated Probe-Solutes at 70-90°C Obtained with Separate Columns Containing the Same Lot of R-45M

	$V_g^o/cm^3\ g^{-1}$								
	70°C			80°C			90°C		
Solute	Column A[a]	Column B[b]	Column C[b]	Column A[a]	Column B[b]	Column C[b]	Column A[a]	Column B[b]	Column C[b]
n-Pentane	17.76	17.72	17.76	-	13.90	13.70	-	11.00	11.01
n-Hexane	42.02	42.05	42.00	-	31.49	31.10	-	24.04	23.79
n-Heptane	98.63	98.10	98.42	-	70.76	69.77	-	52.14	51.93
n-Octane	224.4	226.4	226.7	-	154.8	153.4	-	109.1	108.4
3-Methylpentane	34.84	35.52	35.49	-	27.82	27.42	-	21.42	21.04
2,3-Dimethylpentane	73.47	76.80	77.25	-	56.38	55.47	-	41.99	41.28
3-Methylhexane	75.60	79.15	79.24	-	57.77	57.13	-	42.81	42.10
3-Methylheptane	-	177.1	177.8	-	123.2	122.6	-	87.71	87.11
1-Hexene	42.33	42.15	42.06	-	31.92	31.49	-	24.40	24.17
1-Heptene	98.12	98.34	98.12	-	70.62	69.98	-	52.00	51.60
1-Octene	224.6	226.2	226.5	-	155.1	153.9	-	110.0	109.0
Benzene	117.4	117.1	117.8	-	86.53	86.36	-	65.09	64.89
Toluene	283.3	283.4	286.6	-	200.7	201.0	-	144.3	144.3
Ethylbenzene	595.6	595.0	595.5	-	-	400.0	-	277.2	279.6
Cyclohexane	91.63	91.55	91.25	-	67.48	66.76	-	50.87	50.55
Methylcyclohexane	146.2	147.1	146.1	-	105.6	104.7	-	78.10	77.55
Tetrahydrofuran	95.57	98.40	97.24	-	71.98	70.60	-	52.49	52.37
Thiophene	137.8	140.2	140.9	-	103.3	102.2	-	76.47	75.54
Dimethyl Ketone	26.70	27.59	26.98	-	21.40	20.92	-	16.76	16.51
Methyl Ethyl Ketone	63.24	63.93	63.62	-	47.49	47.14	-	35.91	35.62
Methyl Propyl Ketone	132.9	134.7	133.8	-	95.97	95.36	-	69.73	69.59
Methyl Butyl Ketone	-	314.5	311.3	-	214.2	213.7	-	150.4	149.7
Acetylacetone	322.6	321.2	321.3	-	228.2	226.4	-	161.8	159.2

[a] Stationary-phase loading of 9% w/w. [b] Stationary-phase loading of 5% w/w.

TABLE 6. Test of the Detectability of Variations in Batches of R-45M by the Inverse GC Technique: Fully-Corrected Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ for the Indicated Probe-Solutes at 70-90°C Obtained with Columns Containing Separate Lots of R-45M

	$V_g^o/cm^3\ g^{-1}$								
	70°C			80°C			90°C		
Solute	Lot A[a]	Lot B[b]	Lot C[b]	Lot A[a]	Lot B[b]	Lot C[b]	Lot A[a]	Lot B[b]	Lot C[b]
n-Pentane	17.70	17.93	18.24	13.80	13.43	13.74	11.01	10.73	11.03
n-Hexane	42.03	42.95	43.78	31.30	30.47	31.18	23.92	23.33	23.94
n-Heptane	98.26	99.50	102.0	70.27	68.24	69.73	52.04	50.89	51.88
n-Octane	225.6	232.4	237.2	154.1	149.8	153.4	108.8	106.4	109.2
3-Methylpentane	36.51	37.25	36.99	27.62	26.77	27.07	21.23	20.70	21.24
2,3-Dimethylpentane	77.03	77.63	80.33	55.93	54.15	55.78	41.64	40.92	42.00
3-Methylhexane	79.21	77.99	81.30	57.45	54.71	56.73	42.46	41.52	42.68
3-Methylheptane	177.5	182.4	184.7	122.9	119.3	121.8	87.41	85.67	88.12
1-Hexene	42.11	42.16	43.99	31.71	30.34	31.26	24.29	23.48	23.97
1-Heptene	98.23	98.59	101.45	70.30	67.58	69.37	51.80	50.39	51.62
1-Octene	226.4	227.6	235.9	154.5	148.7	152.8	109.5	106.9	108.9
Benzene	117.5	116.3	120.1	86.45	81.02	83.59	64.99	61.18	63.06
Toluene	285.0	286.3	293.2	200.9	188.5	193.9	144.3	136.3	140.6
Ethylbenzene	595.3	601.0	610.6	394.6	379.3	388.8	278.4	265.1	273.7
Cyclohexane	91.40	90.81	94.72	67.09	64.34	66.60	50.71	49.21	50.65
Methylcyclohexane	146.6	147.3	152.4	105.2	100.9	104.1	77.83	75.20	77.41
Tetrahydrofuran	97.82	99.83	101.1	71.29	68.34	68.54	52.43	50.89	50.68
Thiophene	140.6	139.4	144.2	102.8	95.86	98.73	75.96	71.62	73.56
Dimethyl Ketone	28.29	28.23	28.37	21.16	19.92	19.31	16.64	16.08	15.15
Methyl Ethyl Ketone	63.78	62.11	63.27	47.32	43.90	44.03	35.77	33.52	33.20
Methyl Propyl Ketone	134.3	131.5	134.3	95.67	88.91	89.66	69.66	65.58	65.47
Methyl Butyl Ketone	312.9	313.4	316.8	214.0	199.3	201.2	150.1	140.1	141.4
Acetylacetone	321.3	310.4	316.4	227.3	206.9	210.4	160.5	150.9	153.2

[a] Average of columns containing 5% w/w loadings. [b] Stationary-phase loading of 5% w/w.

Graphical Illustration of the Variation of Retentions with Lots of R-45M. Further illustration of the variation of GC retentions with prepolymer properties is shown in Figure 1, which provides the absolute specific retention volumes $V_g^o/cm^3\ g^{-1}$ (80°C) observed with stationary phases comprised of polybutadienes (PBD) of 1000 and 2500 Da; with repeat runs of R-45M obtained from AL (Lot A); and with two of the lots of R-45M received from United Technologies (Lots B and C, respectively). The error bars represent ± 1% on the absolute data.

First, the precision of the data obtained by IGC is illustrated by the repeat runs of AL Lot A. The results show that the reproducibility of the absolute retentions was ca. ± 0.5%, which is commensurate with what can routinely be achieved with the method.

Secondly, the retention of n-octane decreased quite substantially on passing (left to right) from 1000M to 2500M PBD. This is as expected, since retentions are inversely proportional to the stationary-phase molecular weight in the absence of specific energetic interactions. As a result, n-octane eluted after methyl butyl ketone (MBK) and acetylacetone (AcAc) with 1000M PBD, but before these two ketones with 2500M PBD, i.e., there was a reversal in the retention order. The dramatic decrease in the retention of n-octane with AL Lot A was also as expected, since the GPC peak-maximum molecular weight of the latter material is 6800 Da.

Proceeding next from Lot A to Lot B of R-45M, the retention of n-octane increased slightly which indicated that the latter was of slightly lower molecular weight than the former. Similarly, the retention increased again on passing from Lot B to Lot C.

The retentions of each of the ketones increased on passing from PBD to R-45M, which was thought initially to be a reflection of hydrogen-bonding interactions. Further, these appeared to outweigh the effect due to the decrease in the molecular weight of the stationary phase, which would otherwise cause their retentions to decrease. Also, the retention of MBK was about the same with R-45M Lots A and B, that is, the hydroxyl content of each prepolymer appeared to be identical. However, there was a slight increase in the retention of this probe-solute with Lot C, which was taken as indicative of a slightly higher OH content of the latter.

The retention of AcAc decreased sharply on passing from R-45M Lot A to Lot B and, in fact, this solute eluted before MBK with the latter prepolymer. This seemed to suggest that while the hydroxyl content of Lots A and B were virtually identical, there were more adjacent hydroxyls (implying in turn a less-random distribution) in the former material since, otherwise, the specific retention volumes of the solutes would be expected to have been approximately identical. On the other hand, the ketone solutes coeluted with Lot C, which indicated a random spacing of the hydroxyls with this prepolymer.

In contrast, the retentions of the aromatic hydrocarbons (not shown) were found to be roughly equal for the two lots of PBD, yet decreased on passing to R-45M. THF and the ketones also exhibited near-identical retentions with PBD, but each showed an increase with R-45M, indicative of the hydroxyl content of the latter. Thiophene, on the other hand, exhibited the opposite trend, that is, a decrease in V_g^o with hydroxy-terminated polybutadiene.

Inverse Capillary-Column Gas Chromatography of Bulk and Fractionated R-45M. Also evaluated in the preliminary portion of the work were glass-capillary columns with R-45M. Table 7 summarizes the solute retention indices I obtained for all columns containing stationary phases of bulk lot A of R-45M, from which several fractions were derived (see later), as well as two of those fractions, 2A (low molecular weight) and 9A (high molecular weight), at 42° and 52°C. Also shown for comparison are the data obtained for a separate batch of bulk R-45M prepolymer, lot B, which was chosen at random from those available in this Laboratory.

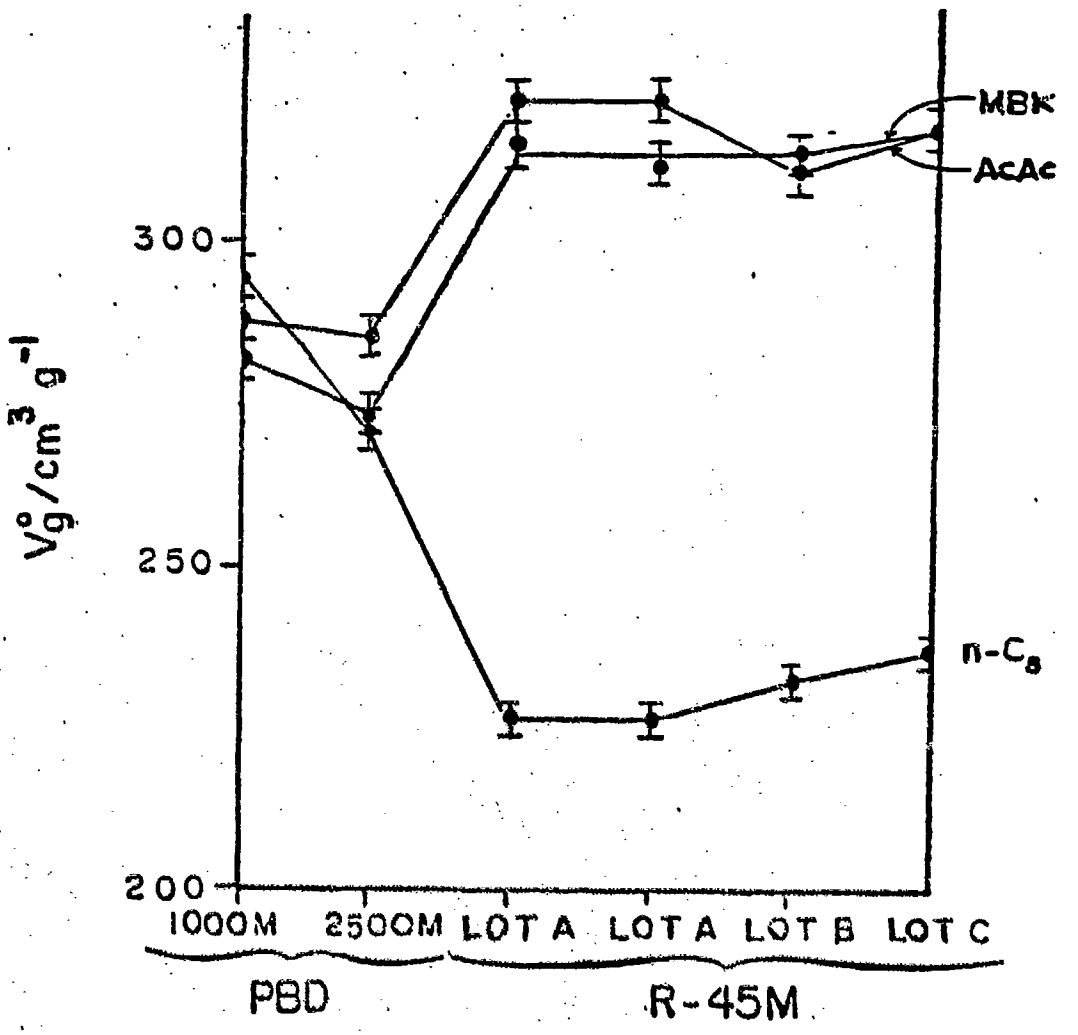

FIGURE 1. Plots of probe-solute specific retention volumes $V_g^o/cm^3\ g^{-1}$ obtained with various lots of polybutadienes (PBD) and hydroxy-terminated polybutadienes (R-45M).

TABLE 7. Retention Indices I for Indicated Solutes with Capillary Columns Containing Fractions 2A and 9A, and Two Bulk Lots of R-45M

	Fraction 2A		Fraction 9A		Bulk Lot A		Bulk Lot B	
Solute	42°C	52°C	42°C	52°C	42°C	52°C	42°C	52°C
Cyclohexane	683.6	686.8	684.3	686.3	684.2	685.4	681.9	686.3
Methylcyclohexane	739.3	740.9	739.5	742.9	740.9	741.5	739.3	740.9
Benzene	716.9	720.6	713.0	716.3	713.7	717.3	725.4	712.1
Toluene	822.8	827.6	818.6	822.5	819.6	823.4	817.0	820.6
Ethylbenzene	911.2	915.7	907.0	911.2	907.8	911.8	905.4	909.7
n-Propanol	722.7	711.3	664.1	655.4	684.2	674.8	681.9	670.4
n-Butanol	827.7	817.2	768.3	760.8	790.1	781.0	786.3	776.3
n-Pentanol	932.9	923.2	873.3	866.0	895.1	886.4	891.5	882.1
2-Butanone	664.7	667.5	641.3	642.0	653.0	653.2	644.9	646.9
2-Pentanone	752.5	754.2	729.2	729.2	740.9	740.9	734.3	735.5
2-Hexanone	- -	-	-	842.3	842.3	836.2	837.4	

It was found, first, that fraction 2A formed droplets immediately upon being coated onto surfaces that had been treated/deactivated in the usual way with hexamethyldisilazane (HMDS), despite taking great care with the temperature control (droplet formation can be caused among other things by ballistic changes in the column temperature). We therefore changed to Carbowax deactivation of the column walls in the hope that surfaces treated with this material would be wetted more readily by R-45M. However, this alternative was only partially successful: column temperatures of in excess of 75°C still resulted in droplet formation with fraction 2A (although not with 9A nor with bulk R-45M prepolymers). Therefore, pending development of a better column deactivation reagent, all probe-solute retentions were measured with freshly-prepared Carbowax-deactivated columns at temperatures not exceeding 55°C.

The retentions with fractionated R-45M exhibited quite remarkable shifts, not only from one phase to another, but from one temperature to another as well. For example, the elution order of benzene and n-propanol with fraction 2A was reversed on passing from 42° to 52°C. The same was also true for toluene and n-butanol. In addition, the alcohols were retained considerably longer with fraction 2A than with 9A, which may be a consequence of the higher equivalent weight of hydroxyl in the former prepolymer material (however, see later).

Comparison of the retention indices with bulk prepolymers A and B showed that cyclohexane and n-propanol overlapped completely with both at 42°C, but were well resolved with each solvent at 52°C. Also, the retention indices of cyclohexane were nearly temperature-invariant whereas, in marked contrast, those for n-propanol were 684.2 and 681.9 with lots A and B respectively at 42°C, but which then decreased to 674.8 and 670.4 on passing to 52°C. These data are most likely a reflection of the hydrogen bonding extant between the latter solute and each of the bulk prepolymer stationary phases, where the equilibrium constants for the respective interactions (hence the solute retentions) decrease with increasing temperature. On the other hand, athermal dispersive forces largely govern the retentions of the alicyclic hydrocarbon and so, its retention indices remained approximately constant over the temperature range considered.

In any event, these preliminary results indicated that inverse capillary-column GC held some promise as a prepolymer characterization technique: the solute retentions were obviously extremely sensitive to changes in the stationary phase, including functionality and, presumably, molecular weight and branching as well. The information content of the probe-solute retentions was, potentially, therefore quite substantial.

Summary of Preliminary Findings. Overall, the preliminary findings indicated that the inverse GC technique, coupled with appropriate probe-solutes, held considerable promise for the characterization of R-45M: one need simply make a GC column of the material, and then derive the information desired directly from the retentions of probe-solutes. That is, there was the likely possibility that nomographs could be derived with which molecular weight, functionality, and chain-branching could be determined simply by injecting a bank of appropriate probe-solutes onto a column that was thermostated at a specified temperature and that contained the prepolymer as a stationary phase. Further, such a set of nomographs could in principle be based solely upon solute capacity factors, which in turn could be calculated directly from strip-chart recordings. In addition, the technique would be applicable to any prepolymer system so long as the latter could be used as a stationary phase. However, in order to derive information of this type, it would first be necessary to correlate quantitatively the solute retentions with the properties of interest. For example, in order to delineate the effects of molecular weight, closely-fractionated and well-characterized prepolymer would be required, followed by the determination at high levels of precision and accuracy of the absolute retentions of what were thought to be appropriate probe-solutes. A nomograph of molecular weight as a function of retentions could then be defined.

An indication of the likely success of such a treatment obtained in this portion of the work is shown in Table 8, where the data have been cast in the form of a comparison of the specific retention volumes of the bank of probe-solutes with 1000M and 2500M PBD together with those of Table 6, viz., R-45M. The trends provided strong indication at this point that it did indeed appear to be possible to speciate at least molecular weight and hydroxyl content with suitable probe-solutes and, with further exploratory work, perhaps chain branching as well.

Specific Retention Volumes and Retention Indices with Standard Lots of R-45M

The specific retention volumes; the van't Hoff slopes m, intercepts -b, and linear least-squares correlation coefficients r for the regression of $\ln V_g^o$ against $10^3\ T^{-1}/K^{-1}$ (taken over the temperature range 30-80°C); and the retention indices I of 30 probe-solutes, including normal, branched, alicyclic, olefinic, aromatic, heterocyclic, hetero-functional, and haloalkanes, including ketones, a diketone, and two nitriles, all with the standard lots of R-45M listed in Table 1, are presented below in Tables 9-14. The solute I vary substantially less than the absolute retentions as a function of T and so, are provided only at every other temperature used in the work.

Precision of the Temperature Regressions. The van't Hoff plots should be linear over the 50° temperature-span used here, since it could hardly be expected that the solute heats of solution, i.e., the slopes of the plots, would be temperature-dependent over such a narrow range. Thus, the least-squares correlation coefficients r offer a measure of the precision of the GC data, values less than 0.999 representing significant deviations.

It was found that, in fact, the correlation coefficients were greater than 0.9995 in nearly all instances, and, in most, were substantially better than this. Even so, correlation coefficients of as low as 0.99 were obtained in a few cases. There were subsequently found to be two sources of imprecision, viz., solute volatility (i.e., very short retention times), and gas-liquid interfacial adsorption (leading amongst other things to peak-tailing and irreproducibility of retentions). For example, n-pentane with Poly bd X-10LM had a correlation coefficient of only 0.999, a consequence of the short retention times of this compound with this stationary phase. As the retentions lengthened, however, r improved, passing from 0.9992 for n-hexane to 0.9994 for n-octane. In other cases, e.g., methyl butyl ketone with X-120HM, r was only 0.994. This was a result of gas-liquid interfacial adsorption and asymmetric peak shapes (i.e., a nonlinear sorption isotherm), for which retention times will vary somewhat depending upon the amount of solute injected. The effect was readily apparent with the relatively insensitive thermal conductivity detectors employed in this work, where the injection of a few tenths of a microliter of vapor was required in order to obtain a measurable peak maximum. (An FID, which is several orders of magnitude more sensitive than a TCD, would of course help to overcome this problem.) Even so, the smoothed data are expected to be quite close to the values that would be obtained were Henry's law to be obeyed.

Reproducibility of the Absolute Retentions. Tables 11 and 12 provide the retentions obtained with replicate columns containing X-20LM stationary phase. The reproducibility of the absolute values is excellent for the hydrocarbon solutes, the agreement falling everywhere to within ± 1.5%. However, the haloalkanes, ketones, and nitriles deviate somewhat from this. For example, butyronitrile gives a specific retention volume at 30°C of 657.7 with the first run, yet a value of 632.7 for the second run. This is another consequence of the interfacial effects mentioned above, and serves to emphasize once again that the absolute minimum detectable amounts of solutes of these types must be injected in order to obtain reproducible retentions.

TABLE 8. Comparison of the Probe-Solute Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ with 1000M and 2500M PBD with the Averaged Values (5% w/w Liquid *Loadings; Column A of Table 6)* with R-45M Stationary Phase at 70-90°C

	$V_g^o/cm^3\ g^{-1}$								
	70°C			80°C			90°C		
Solute	1000M PBD	2500M PBD	R-45M	1000M PBD	2500M PBD	R-45M	1000M PBD	2500M PBD	R-45M
n-Pentane	21.94	20.48	17.70	17.09	16.21	13.80	13.57	12.85	11.01
n-Hexane	52.86	49.23	42.03	39.32	36.89	31.30	30.10	28.14	23.92
n-Heptane	125.0	116.2	98.26	89.59	83.70	70.27	66.04	61.54	52.04
n-Octane	295.5	271.1	226.6	201.6	185.9	154.1	142.1	130.4	108.8
3-Methylpentane	46.11	42.42	36.51	34.76	32.36	27.62	26.65	25.37	21.23
2,3-Dimethylpentane	98.02	90.67	77.03	71.36	66.11	55.93	53.13	49.29	41.64
3-Methylhexane	101.0	93.43	79.21	73.34	68.08	57.45	54.59	50.51	42.46
3-Methylheptane	230.9	211.5	177.5	160.2	147.5	122.9	114.7	105.0	87.41
1-Hexene	51.30	48.36	42.11	38.42	36.57	31.71	29.44	28.05	24.29
1-Heptene	121.3	113.9	98.23	86.87	82.00	70.30	63.92	60.46	51.80
1-Octene	284.7	264.6	226.4	195.0	182.1	154.5	138.1	129.1	109.5
Benzene	125.4	126.9	117.5	91.71	93.41	86.45	68.93	70.03	64.99
Toluene	311.3	311.6	285.0	216.9	218.5	200.9	156.0	156.8	144.3
Ethylbenzene	658.8	654.4	595.3	442.9	444.9	394.6	310.2	306.9	278.4
Cyclohexane	109.3	106.2	91.40	80.56	78.64	67.09	60.76	59.24	50.71
Methylcyclohexane	179.8	171.5	146.6	129.1	123.9	105.2	95.38	91.27	77.83
Tetrahydrofuran	85.93	87.21	97.82	62.90	63.66	71.29	48.09	47.28	52.43
Thiophene	144.4	148.8	140.6	105.1	107.9	102.8	78.12	80.39	75.96
Dimethyl Ketone	22.45	22.15	26.29	17.40	17.43	21.16	14.04	13.60	16.64
Methyl Ethyl Ketone	54.71	54.04	63.78	40.70	40.36	47.32	31.16	30.44	35.77
Methyl Propyl Ketone	118.2	115.6	134.3	84.46	82.90	95.67	62.39	60.60	69.66
Methyl Butyl Ketone	282.0	273.5	312.9	192.5	187.5	214.0	136.2	131.2	150.1
Acetylacetone	288.1	285.8	321.3	198.5	197.9	227.3	141.8	140.1	160.5

TABLE 9. Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$; van't Hoff Slopes m, Intercepts b, and Least-Squares Regression Correlation Coefficients r; and Retention Indices I for Listed Probe Solutes at Indicated Temperatures with Poly bd X-10LM R-45M

	$V_g^o/cm^3\ g^{-1}$									I		
Solute	30°C	40°C	50°C	60°C	70°C	80°C	m	- b	r	30°C	50°C	70°C
n-Pentane	46.74	34.77	26.35	20.30	15.88	12.60	2.807	5.416	0.9989_0	(500.0)	(500.0)	(500.0)
n-Hexane	136.4	95.65	68.57	50.15	37.36	28.29	3.368	6.194	0.9991_9	(600.0)	(600.0)	(600.0)
n-Heptane	391.1	259.5	176.7	123.1	87.58	63.52	3.891	6.868	0.9992_7	(700.0)	(700.0)	(700.0)
n-Octane	1108.	695.0	448.6	297.3	201.8	140.0	4.430	7.602	0.9994_0	(800.0)	(800.0)	(800.0)
3-Methylpentane	112.2	80.33	58.70	43.71	33.11	25.48	3.174	5.750	0.9996_2	582.3	584.1	586.1
2,3-Dimethyl-pentane	285.7	194.1	135.1	96.10	69.72	51.51	3.668	6.445	0.9998_7	670.9	672.3	674.0
3-Methylhexane	298.4	201.6	139.5	98.71	71.26	52.41	3.724	6.587	0.9998_3	675.0	675.7	676.5
3-Methylheptane	821.6	524.3	344.0	231.5	159.4	112.1	4.264	7.355	0.9998_1	771.0	771.2	771.5
1-Hexene	136.4	95.65	68.57	50.15	37.36	28.29	3.368	6.194	0.9991_9	600.8	600.6	600.4
1-Heptene	393.7	262.2	179.1	125.2	89.35	64.99	3.857	6.747	0.9993_0	701.2	702.2	703.2
1-Octene	1110.	698.9	452.7	301.0	205.0	142.7	4.393	7.480	0.9993_6	799.5	800.3	801.2
Benzene	473.1	318.9	220.2	155.5	112.0	82.24	3.746	6.199	0.9998_2	718.7	724.0	729.9
Toluene	1409.	899.2	590.0	397.0	273.4	192.3	4.265	6.818	0.9998_7	822.1	828.3	835.1
Ethylbenzene	3393.	2083.	1318.	857.4	571.8	390.2	4.631	7.147	0.9999_7	905.4	913.4	922.1
o-Xylene	5023.	3041.	1899.	1220.	803.9	542.5	4.765	7.198	0.9999_9	942.6	952,0	962.3
p-Xylene	3862.	2358.	1484.	960.2	637.3	432.9	4.686	7.198	0.9999_9	917.7	925.9	934.9
Cyclohexane	315.2	217.5	153.6	110.8	81.40	60.88	3.521	5.861	0.9991_9	680.2	685.9	692.2
Methylcyclo-hexane	562.9	377.3	259.3	182.2	130.7	95.56	3.797	6.192	0.9991_8	735.1	741.3	748.1
Tetrahydrofuran	472.0	317.1	218.3	153.7	110.4	80.86	3.778	6.304	0.9999_0	718.4	723.1	728.2
Thiophene	586.6	392.6	269.4	189.1	135.5	98.91	3.811	6.199	0.9997_9	739.0	745.4	752.3
Acetone	115.9	82.68	60.23	44.71	33.78	25.92	3.206	5.824	0.9988_9	585.4	586.9	588.5
Methyl Ethyl Ketone	309.3	211.6	148.2	106.0	77.36	57.46	3.604	6.155	0.9981_1	678.4	682.1	686.2
Methyl Propyl Ketone	807.5	499.6	318.4	208.5	139.9	96.03	4.559	8.345	0.9973_3	769.3	763.0	756.1
Methyl Butyl Ketone	2170.	1332.	842.4	547.7	365.1	249.0	4.636	7.609	0.9993_7	863.0	866.0	869.2
Acetylacetone	2114.	1317.	845.3	557.1	376.2	259.7	4.489	7.153	0.9999_3	860.5	866.3	872.7
Methylene Chloride	137.0	96.96	70.10	51.68	38.78	29.58	3.282	5.908	0.9998_4	601.2	602.9	604.8
Chloroform	382.3	265.8	175.5	123.1	88.18	64.37	3.814	6.636	0.9998_3	698.4	700.0	701.7
1-Chloropentane	980.6	626.2	411.1	276.8	190.7	134.2	4.258	7.157	0.9997_0	787.7	790.1	792.7
Butyronitrile	708.8	460.0	306.7	209.5	146.3	104.3	4.104	6.974	0.9999_4	757.0	759.0	761.4
Valeronitrile	2014.	1235.	780.0	506.5	337.3	229.9	4.647	7.722	0.9993_0	856.0	857.3	860.0

TABLE 10. Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$; van't Hoff Slopes m, Intercepts b, and Least-Squares Regression Correlation Coefficients r; and Retention Indices I for Listed Probe Solutes at Indicated Temperatures with with Poly bd X-14LM R-45M

	$V_g^o/cm^3\ g^{-1}$									I		
Solute	30°C	40°C	50°C	60°C	70°C	80°C	m	-b	r	30°C	50°C	70°C
n-Pentane	43.59	32.49	24.66	19.03	14.90	11.84	1.212	2.358	0.9994_8	(500.0)	(500.0)	(500.0)
n-Hexane	129.8	90.55	64.58	46.99	34.84	26.27	3.422	6.420	0.9998_9	(600.0)	(600.0)	(600.0)
n-Heptane	373.7	248.0	168.8	117.6	83.66	60.68	3.892	6.915	0.9997_1	(700.0	(700.0)	(700.0)
n-Octane	1072.	672.2	433.9	287.5	195.1	135.4	4.430	7.637	0.9997_6	(800.0)	(800.0)	(800.0)
3-Methylpentane	105.6	75.41	55.00	40.89	30.92	23.76	3.193	5.873	0.9997_2	581.9	583.5	585.2
2,3-Dimethyl-pentane	262.7	179.2	125.2	89.32	65.02	48.18	3.631	6.407	0.9997_7	667.4	669.5	671.7
3-Methylhexane	281.0	189.7	131.3	92.84	67.01	49.26	3.728	6.659	0.9997_0	673.7	674.4	675.2
3-Methylheptane	780.9	498.1	326.7	219.8	151.3	106.4	4.269	7.420	0.9997_2	769.6	769.7	770.0
1-Hexene	131.1	92.31	66.27	48.58	36.23	27.52	3.343	6.151	0.9995_3	602.2	602.9	603.7
1-Heptene	376.2	250.4	170.9	119.4	85.14	61.89	3.864	6.816	0.9996_8	701.0	702.0	703.1
1-Octene	1070.	672.8	435.5	289.3	196.9	136.9	4.402	7.546	0.9996_9	799.1	799.8	800.6
Benzene	442.5	299.7	208.0	147.5	105.8	78.69	3.697	6.104	0.9998_8	716.3	722.6	729.5
Toluene	1351.	861.2	564.3	379.3	260.9	183.3	4.277	6.900	0.9998_3	821.0	826.9	833.4
Ethylbenzene	3228.	1985.	1258.	819.6	547.4	374.1	4.614	7.142	0.9999_7	902.6	910.7	919.6
o-Xylene	4850.	2931.	1828.	1172.	771.7	520.1	4.781	7.283	0.9999_0	940.8	949.8	959.9
p-Xylene	3706.	2262.	1424.	921.4	611.6	415.5	4.685	7.237	0.9999_6	915.6	923.7	932.5
Cyclohexane	299.0	206.3	145.7	105.0	77.20	57.73	3.521	5.914	0.9996_8	679.5	685.3	691.7
Methylcyclo-hexane	538.6	360.5	247.4	173.7	124.4	90.86	3.810	6.281	0.9997_8	734.7	740.7	747.2
Tetrahydrofuran	434.5	290.7	199.4	139.9	100.2	73.17	3.814	6.508	0.9998_9	714.6	718.1	722.0
Thiophene	555.3	371.3	254.6	178.5	127.9	93.26	3.820	6.281	0.9999_2	737.6	743.7	750.4
Acetone	106.4	75.60	54.89	40.63	30.60	23.42	3.240	6.020	0.9997_9	582.6	583.3	584.0
Methyl Ethyl Ketone	291.0	196.5	135.9	96.07	69.32	50.95	3.731	6.635	0.9998_7	677.0	678.0	679.1
Methyl Propyl Ketone	720.2	463.7	306.7	208.0	144.3	102.2	4.181	7.213	0.9999_3	762.0	763.1	764.5
Methyl Butyl Ketone	2036.	1245.	785.3	509.1	338.4	230.3	4.667	7.775	0.9999_8	859.4	861.4	863.7
Acetylacetone	1966.	1227.	788.6	520.4	351.8	243.2	4.475	7.178	0.9999_7	856.1	861.8	868.2
Methylene Chloride	127.1	90.32	65.57	48.53	36.55	27.97	3.241	5.845	0.9997_8	599.3	601.8	604.7
Chloroform	355.2	238.6	164.3	115.7	83.12	60.86	3.777	6.588	0.9998_3	695.7	697.9	700.3
1-Chloropentane	928.3	592.0	388.2	261.1	179.7	126.3	4.271	7.254	0.9998_7	785.8	788.1	790.0
Butyronitrile	653.5	424.7	283.5	193.9	135.5	96.71	4.091	7.013	0.9999_6	752.9	754.9	757.1
Valeronitrile	1847.	1141.	726.2	474.9	318.3	218.2	4.573	7.564	0.9999_9	850.3	853.3	856.5

TABLE 11. Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$; van't Hoff Slopes m, Intercepts b, and Least-Squares Regression Correlation Coefficients r; and Retention Indices I for Listed Probe Solutes at Indicated Temperatures with Poly bd X-20LM R-45M

	$V_g^o/cm^3\ g^{-1}$									I		
Solute	30°C	40°C	50°C	60°C	70°C	80°C	m	- b	r	30°C	50°C	70°C
n-Pentane	49.64	36.72	27.68	21.22	16.52	13.05	2.861	5.533	0.9994_0	(500.0)	(500.0)	(500.0)
n-Hexane	145.9	101.8	72.58	52.83	39.17	29.53	3.420	6.300	0.9997_7	(600.0)	(600.0)	(600.0)
n-Heptane	420.8	276.6	186.4	128.9	91.01	65.52	3.982	7.094	0.9998_5	(700.0)	(700.0)	(700.0)
n-Octane	1207.	747.8	477.3	313.0	210.3	144.6	4.544	7.892	0.9998_6	(800.0)	(800.0)	(800.0)
3-Methylpentane	118.7	84.17	60.95	45.00	33.82	25.83	3.266	5.997	0.9997_1	581.4	582.5	583.7
2,3-Dimethyl-Pentane	297.6	201.1	139.2	98.55	71.17	52.35	3.721	6.578	0.9999_0	667.8	669.6	671.5
3-Methylhexane	318.1	212.8	146.0	102.5	73.41	53.59	3.813	6.816	0.9997_7	674.1	674.6	675.2
3-Methylheptane	879.1	555.4	361.0	240.8	164.5	114.8	4.359	7.600	0.9998_4	769.7	770.0	770.4
1-Hexene	145.7	102.0	73.04	53.36	39.70	30.03	3.381	6.170	0.9998_3	600.6	601.6	602.6
1-Heptene	419.2	277.0	187.8	130.3	92.37	66.77	3.934	6.938	0.9998_4	700.0	701.1	702.2
1-Octene	1191.	742.3	476.6	314.3	212.3	146.6	4.484	7.709	0.9998_9	798.2	799.3	800.5
Benzene	476.3	321.6	222.5	157.4	113.6	83.51	3.728	6.131	0.9998_8	712.0	719.0	726.7
Toluene	1439.	916.3	600.0	403.0	277.0	194.5	4.285	6.864	0.9999_2	816.0	823.6	831.8
Ethylbenzene	3494.	2135.	1344.	870.9	578.5	393.3	4.676	7.268	0.9999_3	899.4	908.6	918.7
o-Xylene	5285.	3164.	1955.	1243.	812.0	543.2	4.871	7.497	0.9999_8	938.4	948.1	958.8
p-Xylene	4051.	2449.	1527.	980.0	645.2	435.0	4.778	7.453	0.9999_9	913.4	922.1	931.1
Cyclohexane	336.9	230.5	161.5	115.6	84.34	62.65	3.602	6.061	0.9997_6	679.5	685.2	691.5
Methylcyclo-hexane	606.7	402.3	273.6	190.4	135.4	98.10	3.901	6.461	0.9998_4	734.8	740.8	747.4
Tetrahydrofuran	466.7	312.3	214.2	150.3	107.7	78.62	3.813	6.434	0.9997_7	710.1	715.0	720.4
Thiophene	581.9	390.9	269.1	189.5	136.2	99.70	3.777	6.094	0.9999_8	730.9	739.1	748.1
Acetone	111.4	80.19	58.89	44.06	33.52	25.90	3.124	5.592	0.9996_2	575.4	578.9	582.5
Methyl Ethyl Ketone	303.9	205.9	143.0	101.4	73.44	54.15	3.693	6.466	0.9999_7	669.8	672.4	675.2
Methyl Propyl Ketone	754.0	485.6	321.3	218.0	151.2	107.1	4.178	7.156	0.9998_9	755.2	757.7	760.4
Methyl Butyl Ketone	2136.	1305.	821.5	531.8	353.1	240.0	4.681	7.774	0.9999_9	853.2	856.7	860.5
Acetylacetone	2012	1257.	808.8	534.3	361.5	250.1	4.464	7.119	0.9999_0	847.5	855.1	863.3
Methylene Chloride	133.2	94.63	68.67	50.80	38.24	29.26	3.245	5.814	0.9999_5	592.2	595.1	598.2
Chloroform	368.9	248.3	171.3	120.8	86.97	63.78	3.758	6.486	0.9999_4	688.0	691.5	695.2
1-Chloropentane	992.4	633.2	415.4	279.5	192.4	135.3	4.266	7.173	0.9999_1	781.1	784.8	788.8
Butyronitrile	657.7	429.2	287.6	197.4	138.5	99.17	4.051	6.874	0.9999_7	742.4	746.1	750.0
Valeronitrile	1853.	1149.	733.8	481.4	323.6	222.5	4.539	7.447	0.9999_7	839.8	844.8	850.2

TABLE 12. Replicate-Column Specific Retention Volumes V_g^o/cm^3 g^{-1}; van't Hoff Slopes m, Intercepts b, and Least-Squares Regression Correlation Coefficients r; and Retention Indices I for Listed Probe Solutes at Indicated Temperatures with Poly bd X-20LM K-45M

	V_g^o/cm^3 g^{-1}									I		
Solute	30°C	40°C	50°C	60°C	70°C	80°C	m	- b	r	30°C	50°C	70°C
n-Pentane	49.91	36.77	27.61	21.09	16.36	12.88	2.901	5.659	0.9997_8	(500.0)	(500.0)	(500.0)
n-Hexane	146.7	101.8	72.27	52.37	38.67	29.05	3.467	6.448	0.9998_4	(600.0)	(600.0)	(600.0)
n-Heptane	421.5	276.0	185.5	127.7	89.85	64.49	4.020	7.216	0.9998_5	(700.0)	(700.0)	(700.0)
n-Octane	1206.	744.6	473.6	309.6	207.4	142.2	4.577	8.004	0.9998_7	(800.0)	(800.0)	(800.0)
3-Methylpentane	118.8	84.14	60.87	44.90	33.72	25.73	3.276	6.028	0.9997_7	581.0	583.5	584.7
2,3-Dimethyl-pentane	297.5	201.0	139.1	98.44	71.08	52.28	3.723	6.586	0.9998_0	667.5	670.4	672.8
3-Methylhexane	316.6	211.9	145.4	102.0	73.11	53.38	3.812	6.816	0.9997_2	673.4	675.0	676.2
3-Methylheptane	873.6	552.3	359.2	239.8	163.9	114.4	4.352	7.585	0.9997_5	769.1	770.0	771.6
1-Hexene	147.0	102.5	73.11	53.21	39.45	29.75	3.421	6.293	0.9997_1	601.1	602.8	603.2
1-Heptene	420.6	276.9	187.0	129.4	91.41	65.88	3.970	7.053	0.9998_2	700.2	701.4	702.5
1-Octene	1195.	740.6	472.8	310.0	208.4	143.2	4.542	7.898	0.9999_4	798.6	798.9	799.9
Benzene	470.8	318.1	220.2	155.8	112.5	82.78	3.722	6.123	0.9997_5	710.8	718.6	727.1
Toluene	1424.	906.6	593.7	398.8	274.2	192.6	4.283	6.869	0.9998_3	815.1	822.8	832.4
Ethylbenzene	3383.	2080.	1318.	858.6	573.3	391.7	4.617	7.102	0.9999_3	896.7	906.6	919.5
o-Xylene	5087.	3070.	1912.	1225.	805.5	542.4	4.793	7.275	0.9999_4	935.1	945.7	959.7
p-Xylene	3935.	2392.	1500.	967.0	639.7	433.1	4.725	7.308	0.9999_0	910.9	920.2	932.5
Cyclohexane	336.7	230.2	161.1	115.2	84.04	62.39	3.609	6.087	0.9997_8	679.2	685.8	692.6
Methylcyclo-hexane	605.9	401.6	273.1	190.0	135.1	97.88	3.904	6.470	0.9998_1	734.6	741.2	748.7
Tetrahydrofuran	460.0	306.6	209.5	146.5	104.6	76.10	3.852	6.576	1.	708.6	713.4	718.5
Thiophene	579.3	388.5	267.0	187.7	134.7	98.46	3.795	6.155	0.9998_0	730.3	738.9	748.4
Acetone	108.7	77.53	56.46	41.91	31.66	24.30	3.208	5.894	0.9998_8	572.6	575.6	577.2
Methyl Ethyl Ketone	299.8	202.7	140.4	99.40	71.81	52.84	3.717	6.558	0.9999_8	668.3	671.3	674.0
Methyl Propyl Ketone	743.4	478.6	316.6	214.7	148.9	105.5	4.182	7.183	0.9999_8	753.9	756.8	760.2
Methyl Butyl Ketone	2115.	1290.	810.9	524.2	347.6	236.0	4.696	7.833	0.9999_7	852.4	855.6	860.4
Acetylacetone	1964.	1234.	797.8	530.0	360.0	250.1	4.412	6.971	0.9999_2	845.4	853.9	864.5
Methylene Chloride	130.6	93.09	67.75	50.26	37.93	29.09	3.215	5.735	0.9999_3	589.9	594.8	598.6
Chloroform	364.7	245.7	169.6	119.7	86.26	63.31	3.749	6.468	0.9999_0	686.7	691.2	695.7
1-Chloropentane	983.3	627.9	412.1	277.4	191.0	134.4	4.262	7.169	0.9998_6	780.2	784.5	789.6
Butyronitrile	632.7	415.8	280.5	193.7	136.7	98.41	3.984	6.693	0.9999_7	738.7	744.0	750.1
Valeronitrile	1837.	1138.	726.0	475.8	319.7	219.6	4.548	7.487	0.9999_1	839.1	843.9	850.5

TABLE 13. Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$; van't Hoff Slopes m, Intercepts b, and Least-Squares Regression Correlation Coefficients r; and Retention Indices I for Listed Probe Solutes at Indicated Temperatures with Poly bd X-25LM R-45M

	$V_g^o/cm^3\ g^{-1}$									I		
Solute	30°C	40°C	50°C	60°C	70°C	80°C	m	-b	r	30°C	50°C	70°C
n-Pentane	47.57	35.02	26.27	20.05	15.54	12.22	2.910	5.735	0.9991_7	(500.0)	(500.0)	(500.0)
n-Hexane	130.1	92.70	67.43	49.99	37.72	28.91	3.221	5.757	0.9999_0	(600.0)	(600.0)	(600.0)
n-Heptane	402.2	265.5	179.8	124.6	88.26	63.74	3.945	7.015	0.9995_3	(700.0)	(700.0)	(700.0)
n-Octane	1155.	718.9	460.7	303.2	204.4	141.0	4.504	7.606	0.9996_4	(800.0	(800.0)	(800.0)
3-Methylpentane	113.6	80.62	58.42	43.16	32.45	24.80	3.260	6.019	0.9996_3	583.4	583.8	584.3
2,3-Dimethyl-pentane	283.6	192.4	133.7	94.93	68.77	50.74	3.685	6.507	0.9996_3	669.0	670.3	671.8
3-Methylhexane	303.9	204.0	140.4	98.79	70.96	51.93	3.783	6.762	0.9995_9	675.4	675.4	675.5
3-Methylheptane	838.7	532.7	347.9	233.2	159.9	112.1	4.310	7.485	0.9997_0	770.3	770.2	770.1
1-Hexene	139.7	98.09	70.41	51.56	38.46	29.15	3.355	6.128	0.9995_0	602.8	603.3	604.1
1-Heptene	402.5	266.8	181.4	126.2	89.70	65.00	3.904	6.881	0.9996_5	701.7	702.1	702.8
1-Octene	1145.	716.2	461.2	304.9	206.5	145.0	4.455	7.651	0.9996_6	799.4	799.6	800.0
Benzene	461.6	311.9	216.0	152.9	110.4	81.21	3.721	6.139	0.9998_4	714.5	720.4	727.0
Toluene	1401.	892.3	584.5	392.7	270.1	189.7	4.281	6.876	0.9998_6	818.3	824.3	831.3
Ethylbenzene	3354.	2059.	1303.	847.9	565.5	386.0	4.629	7.153	0.9999_6	899.9	908.0	917.4
o-Xylene	5034.	3038.	1891.	1212.	796.6	536.3	4.794	7.292	0.9999_8	937.8	946.9	957.3
p-Xylene	3859.	2352.	1479.	955.1	633.1	429.5	4.701	7.249	0.9999_6	913.0	921.8	930.6
Cyclohexane	322.1	221.0	155.2	111.3	81.39	60.58	3.570	6.027	0.9996_6	680.9	685.9	691.5
Methylcyclo-hexane	580.4	386.3	263.7	184.2	131.4	95.49	3.864	6.382	0.9997_3	735.9	741.2	747.3
Tetrahydrofuran	433.6	290.4	199.4	140.1	100.4	73.38	3.804	6.475	0.9999_2	708.6	712.0	715.9
Thiophene	574.8	384.1	263.5	184.9	132.5	96.72	3.813	6.226	0.9998_5	734.9	741.1	748.3
Acetone	107.7	75.96	54.74	40.23	30.10	22.90	3.315	6.256	0.9996_4	578.4	577.0	575.5
Methyl Ethyl Ketone	292.5	196.5	135.2	95.22	68.42	50.09	3.778	6.785	0.9998_7	671.8	671.5	671.2
Methyl Propyl Ketone	725.3	464.6	305.9	206.6	142.7	100.7	4.228	7.361	0.9998_5	756.7	756.7	756.9
Methyl Butyl Ketone	2047.	1245.	781.1	503.9	333.5	225.9	4.719	7.942	0.9999_2	853.7	854.6	855.8
Acetylacetone	1972.	1224.	782.3	513.7	345.7	237.9	4.528	7.351	0.9999_0	850.2	854.8	860.0
Methylene Chloride	129.4	92.02	66.82	49.46	37.26	28.52	3.239	5.820	0.9996_8	595.6	597.9	600.4
Chloroform	361.0	242.7	167.2	117.8	84.68	62.03	3.771	6.551	0.9998_0	691.5	693.6	696.1
1-Chloropentane	950.2	609.4	401.8	271.6	187.8	132.7	4.216	7.050	0.9998_6	782.0	785.2	788.9
Butyronitrile	634.3	413.5	276.7	189.7	133.0	95.11	4.063	6.950	0.9999_4	744.2	746.2	748.7
Valeronitrile	1794.	1109.	706.6	462.5	310.3	212.9	4.563	7.559	0.9999_9	841.4	844.2	847.4

TABLE 14. Specific Retention Volumes V_g^o/cm^3 g^{-1}; van't Hoff Slopes m, Intercepts b, and Least-Squares Regression Correlation Coefficients r; and Retention Indices I for Listed Probe Solutes at Indicated Temperatures with Poly bd X-120HM R-45M

Solute	V_g^o/cm^3 g^{-1}									I		
	30°C	40°C	50°C	60°C	70°C	80°C	m	-b	r	30°C	50°C	70°C
n-Pentane	47.28	33.90	24.82	18.51	14.05	10.83	3.156	6.556	0.9939_7	(500.0)	(500.0)	(500.0)
n-Hexane	140.6	94.96	65.69	46.46	33.53	24.65	3.729	7.354	0.9954_6	(600.0)	(600.0)	(600.0)
n-Heptane	406.4	259.1	169.9	114.2	78.63	55.27	4.272	8.084	0.9964_4	(700.0)	(700.0)	(700.0)
n-Octane	1156.	696.8	433.4	277.4	182.2	122.5	4.805	8.798	0.9971_9	(800.0)	(800.0)	(800.0)
3-Methylpentane	109.4	77.92	56.68	42.02	31.70	24.30	3.222	5.932	0.9994_5	577.7	585.6	594.4
2,3-Dimethyl-pentane	273.8	186.5	130.1	92.74	67.42	49.91	3.644	6.410	0.9995_3	663.8	672.8	682.8
3-Methylhexane	292.4	197.3	136.4	96.37	69.50	51.06	3.737	6.648	0.9995_1	670.0	677.7	686.3
3-Methylheptane	807.7	515.8	337.6	227.0	156.2	109.8	4.273	7.400	0.9995_8	765.4	772.9	781.2
1-Hexene	141.7	95.73	66.26	46.88	33.85	24.89	3.724	7.330	0.9947_1	602.0	602.0	602.1
1-Heptene	389.4	256.5	173.9	120.5	85.32	61.60	3.948	7.059	0.9997_0	696.8	703.3	710.3
1-Octene	1112.	691.0	442.2	290.6	195.7	134.8	4.518	7.890	0.9997_4	795.4	801.2	807.6
Benzene	449.2	302.4	208.6	147.1	105.9	77.69	3.757	6.286	0.9998_5	710.3	722.3	735.7
Toluene	1361.	863.6	563.5	377.2	258.5	181.0	4.320	7.034	0.9998_8	814.4	826.6	840.1
Ethylbenzene	3244.	1987.	1254.	813.9	541.7	368.9	4.655	7.270	0.9999_4	895.9	910.6	926.7
o-Xylene	4973.	2976.	1838.	1169.	763.1	510.4	4.875	7.569	0.9998_7	936.0	950.7	966.9
p-Xylene	3825.	2309.	1439.	922.0	606.4	408.5	4.789	7.548	0.9998_3	819.5	834.3	940.0
Cyclohexane	326.1	216.0	146.8	102.1	72.54	52.54	3.909	7.108	0.9952_3	680.2	685.5	691.3
Methylcyclo-hexane	585.8	376.8	249.1	168.8	117.0	82.84	4.188	7.443	0.9958_8	735.2	741.0	747.3
Tetrahydrofuran	383.8	256.3	175.5	122.9	87.89	64.05	3.834	6.696	0.9999_2	695.5	704.2	713.8
Thiophene	561.8	373.5	254.6	177.6	126.5	91.88	3.877	6.458	0.9998_7	731.3	743.2	756.5
Acetone	100.4	69.52	49.23	35.59	26.22	19.66	3.492	6.910	0.9993_7	569.6	570.8	572.2
Methyl Ethyl Ketone	262.6	174.6	119.1	83.09	59.21	43.01	3.874	7.208	0.9999_9	659.9	663.5	667.6
Methyl Propyl Ketone	646.0	410.1	267.8	179.4	123.0	86.17	4.313	7.758	0.9999_9	744.4	748.6	753.2
Methyl Butyl Ketone	2045.	1161.	682.4	414.2	258.9	166.1	5.374	10.11	0.9940_8	852.6	846.7	840.3
Acetylacetone	1822.	1116.	703.9	456.6	303.7	206.8	4.660	7.863	0.9999_9	841.7	850.0	859.0
Methylene Chloride	127.6	89.48	64.16	46.93	34.96	26.48	3.366	6.255	0.9999_5	592.1	598.6	605.9
Chloroform	353.3	234.9	160.2	111.7	79.62	57.83	3.875	6.915	0.9999_3	687.7	694.6	702.2
1-Chloropentane	931.3	593.1	388.4	260.9	179.4	126.0	4.284	7.294	0.9998_3	778.7	787.6	797.3
Butyronitrile	592.3	379.0	249.4	168.2	116.1	81.87	4.237	7.592	0.9999_8	736.2	741.1	746.5
Valeronitrile	1704.	1030.	642.4	412.1	271.3	182.9	4.779	8.323	0.9999_9	835.5	840.4	845.8

Reproducibility of the Retention Indices. The replicate solute I in Tables 10 and 11 were found to be much more reproducible than were the absolute retentions, deviating by at most 2 or 3 retention-index units. This is as expected, since the indices are, in reality, retentions that are taken relative to those of n-alkanes. Thus, whatever instrumental or system variations there are will be smoothed. Data reduction in terms of retention indices also has the advantage of requiring only raw retention times, as opposed to specific retention volumes, for which the column-volume of stationary phase must be known. That is, retention indices can be calculated from data taken directly from strip-chart recordings and so, enable virtually any system to be employed for inverse GC, including those that make use of capillary columns. However, there is the drawback that information that might otherwise be derived from absolute retentions is thereby lost. The question therefore remained at this point whether the information content of retention-index data was sufficient to permit extraction of the desired physicochemical properties of prepolymers, or whether, in fact, absolute retentions were indeed required.

Variation of the Absolute Retentions with Prepolymer Lot. Figure 2 presents the V_g^o for several representative solutes as a function of the batch of R-45M, where straight lines have been used to connect the data points. There are clearly quite striking changes on passing from one prepolymer to the next. For example, thiophene (Th) is retained longer than methylcyclohexane (MC) with X-14LM, but there is an inversion in the retention order of this solute pair on passing to X-20LM. Also, while the retentions of all other solutes rise on passing between X-14LM and X-20LM (the increase for those of MC being particularly sharp), those of butyronitrile remain nearly constant.

Variation of the Relative Retentions with Prepolymer Lot. The retention indices of the solutes of Figure 2 are presented in Figure 3. A striking difference between the two illustrations is that the retention indices of methylcyclohexane are nearly solvent-independent. Also, those for thiophene are at times less than those for methylcyclohexane, yet increase beyond methylcyclohexane with other stationary phases. Perhaps the most dramatic change of all, however, is the behavior of 3-methylheptane relative to butyronitrile: the retention indices of the former solute tend to increase from X-14LM to X-120HM, whereas those for the latter compound drop very sharply across the same stationary-phase range. The information content of the retention-index data thus appeared at this point to be quite high.

Activity Coefficients

The fully-corrected probe-solute activity coefficients, calculated as described elsewhere (9), are provided below in Tables 15-20.

Thermodynamic Parameters

The Gibbs free energies, entropies, and enthalpies were calculated from the solute specific retention volumes and stationary-phase densities as described elsewhere (21). The results are reported in Tables 21-33.

Fractional Extraction

The amounts extracted for X-25LM as described in the Experimental Section are shown in Figure 4. The quantities corresponded roughly to what was found previously with extraction-solvent step-changes of 5% (10% step-changes were employed in this work). The first fraction, no. 1A, was by far the largest, amounting to close to one-fourth of the total quantity of polymer. Moreover, thereafter, the amounts obtained with each combination of solvents were about equal, viz., 2A and 2B; 3A and 3B, etc.

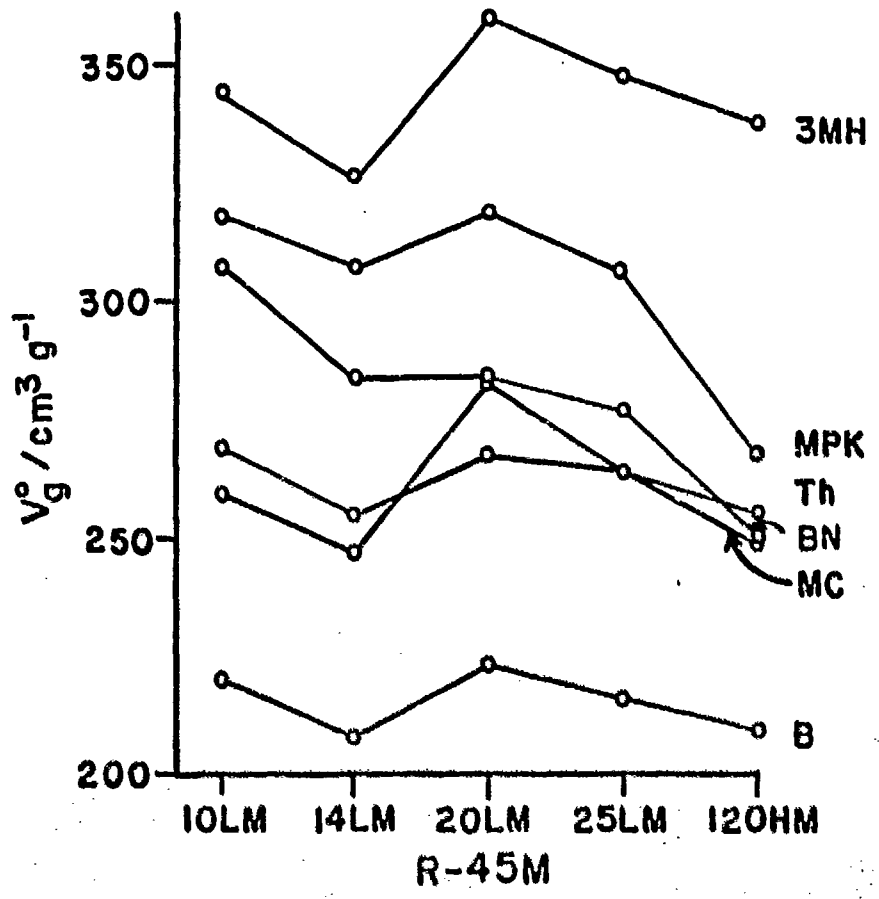

FIGURE 2. Plots of specific retention volume V_g^o data at 50°C obtained with indicated lots of R-45M. Solutes: B, benzene; MC, methylcyclohexane; BN, butyronitrile; Th, thiophene; MPK, methyl propyl ketone; 3MH, 3-methylheptane.

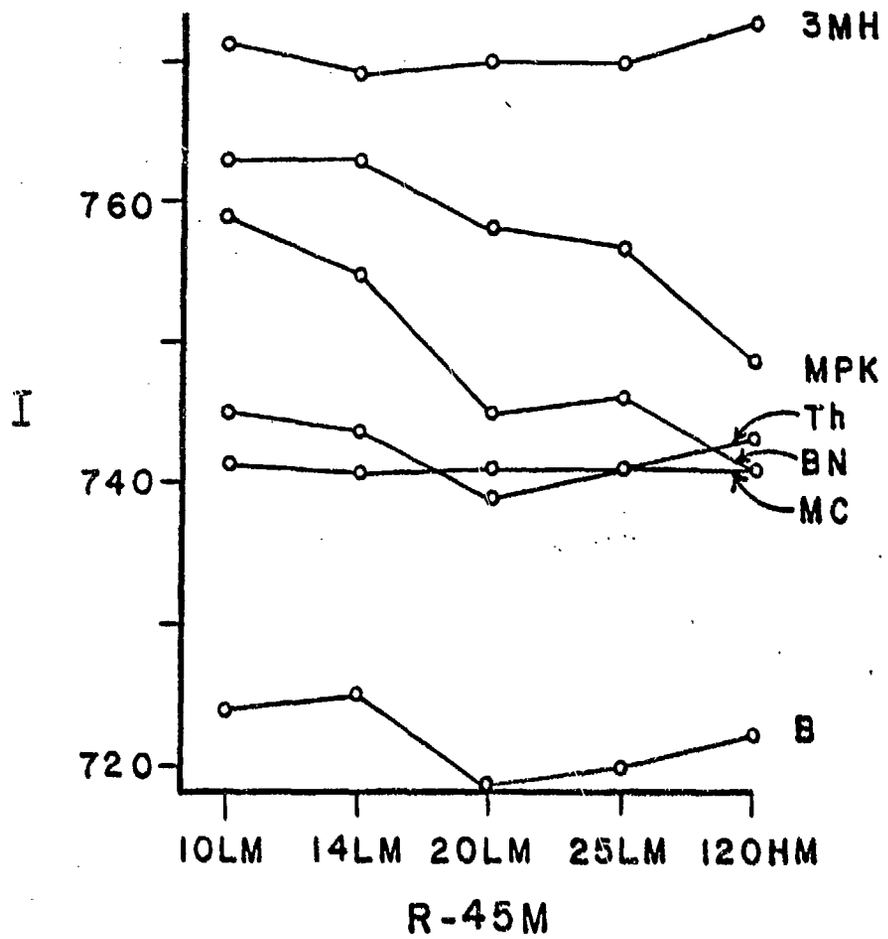

FIGURE 3. As in Figure 2; ordinate of solute retention index I.

TABLE 15. Infinite-Dilution Activity Coefficients γ_A^∞ for Listed Probe Solutes at Indicated Temperatures with Poly bd X-10LM R-45M

	γ_A^∞					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	0.588	0.566	0.548	0.535	0.525	0.518
n-Hexane	0.653	0.627	0.607	0.592	0.581	0.574
n-Heptane	0.723	0.690	0.665	0.646	0.633	0.623
n-Octane	0.804	0.762	0.731	0.708	0.692	0.681
3-Methylpentane	0.641	0.612	0.590	0.573	0.560	0.550
2,3-Dimethyl-pentane	0.670	0.642	0.621	0.606	0.595	0.587
3-Methylhexane	0.713	0.681	0.657	0.638	0.625	0.616
3-Methylheptane	0.786	0.748	0.719	0.699	0.684	0.675
1-Hexene	0.533	0.518	0.507	0.500	0.495	0.493
1-Heptene	0.588	0.566	0.549	0.538	0.530	0.525
1-Octene	0.651	0.624	0.604	0.590	0.581	0.575
Benzene	0.293	0.285	0.279	0.276	0.274	0.273
Toluene	0.319	0.310	0.304	0.301	0.299	0.299
Ethylbenzene	0.384	0.367	0.356	0.347	0.342	0.338
o-Xylene	0.369	0.352	0.340	0.331	0.325	0.322
p-Xylene	0.365	0.351	0.341	0.334	0.330	0.327
Cyclohexane	0.432	0.415	0.401	0.391	0.383	0.378
Methylcyclo-hexane	0.500	0.480	0.464	0.452	0.443	0.437
Tetrahydrofuran	0.175	0.174	0.174	0.175	0.177	0.180
Thiophene	0.280	0.271	0.265	0.260	0.257	0.255
Acetone	0.501	0.474	0.452	0.434	0.419	0.407
Methyl Ethyl Ketone	0.467	0.441	0.420	0.404	0.391	0.382
Methyl Propyl Ketone	0.446	0.445	0.448	0.453	0.460	0.470
Methyl Butyl Ketone	0.489	0.465	0.447	0.433	0.424	0.417
Acetylacetone	0.635	0.596	0.567	0.544	0.527	0.514
Methylene Chloride	0.226	0.220	0.216	0.213	0.211	0.209
Chloroform	0.181	0.184	0.188	0.192	0.197	0.202
1-Chloropentane	0.417	0.405	0.397	0.391	0.387	0.385
n-Butyronitrile	0.858	0.818	0.783	0.753	0.725	0.701
n-Valeronitrile	0.834	0.789	0.754	0.727	0.706	0.690

TABLE 16. Infinite-Dilution Activity Coefficients γ_A^∞ for Listed Probe Solutes at Indicated Temperatures with Poly bd X-14LM R-45M

	γ_A^∞					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	0.461	0.443	0.429	0.418	0.410	0.404
n-Hexane	0.503	0.485	0.472	0.463	0.457	0.453
n-Heptane	0.555	0.529	0.510	0.495	0.485	0.478
n-Octane	0.609	0.577	0.553	0.536	0.524	0.516
3-Methylpentane	0.499	0.478	0.461	0.448	0.439	0.432
2,3-Dimethyl-pentane	0.533	0.510	0.491	0.477	0.467	0.460
3-Methylhexane	0.554	0.530	0.511	0.497	0.487	0.480
3-Methylheptane	0.605	0.576	0.555	0.539	0.528	0.521
1-Hexene	0.406	0.394	0.384	0.378	0.374	0.372
1-Heptene	0.451	0.434	0.422	0.413	0.407	0.404
1-Octene	0.495	0.475	0.460	0.450	0.443	0.439
Benzene	0.230	0.222	0.217	0.213	0.210	0.209
Toluene	0.243	0.237	0.233	0.231	0.230	0.230
Ethylbenzene	0.295	0.282	0.273	0.266	0.261	0.259
o-Xylene	0.280	0.268	0.259	0.253	0.248	0.246
p-Xylene	0.279	0.268	0.260	0.255	0.251	0.250
Cyclohexane	0.334	0.320	0.310	0.302	0.296	0.292
Methylcyclo-hexane	0.383	0.368	0.356	0.347	0.341	0.337
Tetrahydrofuran	0.139	0.139	0.140	0.141	0.143	0.145
Thiophene	0.217	0.210	0.205	0.202	0.199	0.198
Acetone	0.400	0.380	0.363	0.349	0.339	0.330
Methyl Ethyl Ketone	0.364	0.348	0.336	0.327	0.320	0.315
Methyl Propyl Ketone	0.367	0.351	0.340	0.332	0.327	0.324
Methyl Butyl Ketone	0.382	0.364	0.351	0.341	0.335	0.330
Acetylacetone	0.500	0.469	0.445	0.427	0.413	0.402
Methylene Chloride	0.178	0.173	0.169	0.166	0.164	0.162
Chloroform	0.143	0.145	0.147	0.150	0.153	0.157
1-Chloropentane	0.323	0.314	0.308	0.303	0.301	0.300
n-Butyronitrile	0.702	0.649	0.621	0.596	0.574	0.554
n-Valeronitrile	0.666	0.625	0.593	0.568	0.548	0.533

TABLE 17. Infinite-Dilution Activity Coefficients γ_A^∞ for Listed Probe Solutes at Indicated Temperatures with Poly bd X-20LM R-45M

	γ_A^∞					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	0.426	0.413	0.402	0.395	0.389	0.385
n-Hexane	0.470	0.454	0.442	0.433	0.427	0.424
n-Heptane	0.518	0.499	0.486	0.475	0.469	0.466
n-Octane	0.569	0.546	0.529	0.518	0.512	0.508
3-Methylpentane	0.467	0.450	0.438	0.429	0.422	0.418
2,3-Dimethyl-pentane	0.495	0.478	0.465	0.455	0.449	0.445
3-Methylhexane	0.515	0.497	0.483	0.474	0.467	0.464
3-Methylheptane	0.566	0.544	0.528	0.518	0.511	0.508
1-Hexene	0.385	0.374	0.367	0.362	0.359	0.358
1-Heptene	0.425	0.413	0.404	0.398	0.395	0.394
1-Octene	0.468	0.452	0.442	0.435	0.432	0.431
Benzene	0.224	0.218	0.213	0.210	0.208	0.207
Toluene	0.240	0.235	0.231	0.228	0.228	0.228
Ethylbenzene	0.287	0.276	0.269	0.263	0.260	0.259
o-Xylene	0.270	0.261	0.254	0.250	0.248	0.247
p-Xylene	0.268	0.261	0.255	0.252	0.251	0.251
Cyclohexane	0.312	0.301	0.294	0.288	0.285	0.283
Methylcyclo-hexane	0.358	0.347	0.339	0.333	0.330	0.328
Tetrahydrofuran	0.136	0.136	0.137	0.138	0.140	0.142
Thiophene	0.217	0.210	0.204	0.200	0.197	0.195
Acetone	0.402	0.376	0.356	0.339	0.325	0.314
Methyl Ethyl Ketone	0.366	0.349	0.336	0.326	0.318	0.312
Methyl Propyl Ketone	0.368	0.353	0.342	0.334	0.328	0.325
Methyl Butyl Ketone	0.383	0.365	0.353	0.344	0.337	0.333
Acetylacetone	0.514	0.481	0.456	0.437	0.423	0.412
Methylene Chloride	0.179	0.174	0.170	0.167	0.165	0.163
Chloroform	0.145	0.146	0.148	0.151	0.154	0.157
1-Chloropentane	0.318	0.309	0.302	0.298	0.296	0.294
n-Butyronitrile	0.713	0.676	0.644	0.615	0.590	0.568
n-Valeronitrile	0.817	0.653	0.618	0.589	0.567	0.549

TABLE 18. Replicate Measurement of Activity Coefficients γ_A^∞ for Listed Probe Solutes at Indicated Temperatures with Poly bd X-20LM R-45M

	γ_A^∞					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	0.424	0.412	0.403	0.397	0.393	0.391
n-Hexane	0.468	0.454	0.444	0.437	0.433	0.431
n-Heptane	0.517	0.500	0.488	0.480	0.475	0.473
n-Octane	0.569	0.548	0.533	0.524	0.519	0.517
3-Methylpentane	0.466	0.450	0.438	0.429	0.423	0.419
2,3-Dimethyl-pentane	0.496	0.478	0.465	0.456	0.449	0.446
3-Methylhexane	0.518	0.499	0.485	0.476	0.469	0.466
3-Methylheptane	0.569	0.547	0.531	0.520	0.513	0.509
1-Hexene	0.381	0.373	0.367	0.363	0.361	0.362
1-Heptene	0.424	0.413	0.405	0.401	0.399	0.399
1-Octene	0.466	0.454	0.445	0.441	0.440	0.442
Benzene	0.227	0.220	0.215	0.212	0.210	0.209
Toluene	0.243	0.237	0.233	0.231	0.230	0.230
Ethylbenzene	0.296	0.283	0.274	0.267	0.263	0.260
o-Xylene	0.281	0.269	0.260	0.254	0.250	0.248
p-Xylene	0.276	0.267	0.260	0.256	0.253	0.252
Cyclohexane	0.312	0.302	0.295	0.289	0.286	0.284
Methylcyclo-hexane	0.358	0.347	0.339	0.334	0.330	0.329
Tetrahydrofuran	0.138	0.139	0.140	0.142	0.144	0.147
Thiophene	0.218	0.211	0.206	0.202	0.199	0.198
Acetone	0.412	0.389	0.371	0.356	0.344	0.335
Methyl Ethyl Ketone	0.371	0.355	0.342	0.332	0.325	0.320
Methyl Propyl Ketone	0.374	0.358	0.347	0.339	0.333	0.330
Methyl Butyl Ketone	0.387	0.370	0.357	0.349	0.343	0.339
Acetylacetone	0.526	0.490	0.463	0.441	0.424	0.412
Methylene Chloride	0.182	0.177	0.172	0.169	0.166	0.164
Chloroform	0.146	0.148	0.150	0.152	0.155	0.159
1-Chloropentane	0.321	0.311	0.305	0.300	0.298	0.296
n-Butyronitrile	0.741	0.698	0.660	0.627	0.598	0.572
n-Valeronitrile	0.704	0.659	0.624	0.596	0.574	0.557

TABLE 19. Infinite-Dilution Activity Coefficients γ_A^∞ for Listed Probe Solutes at Indicated Temperatures with Poly bd X-25LM R-45M

	γ_A^∞					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	0.368	0.358	0.351	0.346	0.343	0.341
n-Hexane	0.437	0.413	0.394	0.379	0.367	0.358
n-Heptane	0.449	0.431	0.417	0.407	0.401	0.396
n-Octane	0.492	0.470	0.454	0.443	0.436	0.432
3-Methylpentane	0.404	0.389	0.378	0.370	0.364	0.360
2,3-Dimethyl-pentane	0.431	0.414	0.401	0.391	0.385	0.380
3-Methylhexane	0.447	0.429	0.416	0.407	0.400	0.397
3-Methylheptane	0.491	0.470	0.454	0.443	0.435	0.431
1-Hexene	0.332	0.322	0.315	0.310	0.307	0.306
1-Heptene	0.367	0.355	0.346	0.340	0.337	0.335
1-Octene	0.403	0.388	0.378	0.372	0.368	0.366
Benzene	0.192	0.186	0.182	0.179	0.177	0.176
Toluene	0.205	0.199	0.196	0.194	0.193	0.194
Ethylbenzene	0.248	0.237	0.230	0.224	0.220	0.218
o-Xylene	0.235	0.222	0.218	0.213	0.209	0.208
p-Xylene	0.233	0.225	0.219	0.214	0.212	0.210
Cyclohexane	0.270	0.260	0.253	0.248	0.245	0.242
Methylcyclo-hexane	0.310	0.299	0.291	0.285	0.281	0.279
Tetrahydrofuran	0.121	0.121	0.122	0.123	0.124	0.126
Thiophene	0.183	0.177	0.173	0.170	0.168	0.167
Acetone	0.344	0.329	0.317	0.307	0.300	0.294
Methyl Ethyl Ketone	0.315	0.303	0.294	0.287	0.282	0.279
Methyl Propyl Ketone	0.317	0.306	0.297	0.292	0.288	0.286
Methyl Butyl Ketone	0.331	0.317	0.307	0.300	0.296	0.293
Acetylacetone	0.434	0.409	0.391	0.377	0.366	0.358
Methylene Chloride	0.152	0.148	0.145	0.142	0.140	0.138
Chloroform	0.123	0.124	0.126	0.128	0.131	0.134
1-Chloropentane	0.275	0.266	0.259	0.254	0.251	0.249
n-Butyronitrile	0.612	0.581	0.554	0.530	0.509	0.491
n-Valeronitrile	0.597	0.560	0.531	0.508	0.490	0.476

TABLE 20. Infinite-Dilution Activity Coefficients γ_A^∞ for Listed Probe Solutes at Indicated Temperatures with Poly bd X-120HM R-45M

	γ_A^∞					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	0.181	0.181	0.182	0.183	0.185	0.188
n-Hexane	0.198	0.197	0.198	0.199	0.202	0.206
n-Heptane	0.217	0.216	0.216	0.217	0.220	0.223
n-Octane	0.240	0.237	0.236	0.237	0.239	0.243
3-Methylpentane	0.205	0.197	0.191	0.186	0.182	0.180
2,3-Dimethyl-pentane	0.218	0.209	0.201	0.196	0.192	0.189
3-Methylhexane	0.227	0.217	0.209	0.204	0.200	0.197
3-Methylheptane	0.249	0.237	0.229	0.222	0.218	0.215
1-Hexene	0.160	0.161	0.164	0.167	0.171	0.175
1-Heptene	0.185	0.180	0.177	0.174	0.173	0.173
1-Octene	0.203	0.197	0.193	0.191	0.190	0.190
Benzene	0.096	0.094	0.092	0.091	0.090	0.090
Toluene	0.103	0.101	0.099	0.099	0.099	0.099
Ethylbenzene	0.125	0.120	0.117	0.114	0.112	0.112
o-Xylene	0.116	0.112	0.110	0.108	0.107	0.107
p-Xylene	0.306	0.280	0.260	0.245	0.108	0.108
Cyclohexane	0.130	0.130	0.131	0.132	0.134	0.137
Methylcyclo-hexane	0.150	0.150	0.151	0.152	0.154	0.157
Tetrahydrofuran	0.067	0.067	0.068	0.068	0.069	0.071
Thiophene	0.091	0.089	0.087	0.086	0.086	0.086
Acetone	0.181	0.176	0.172	0.170	0.168	0.167
Methyl Ethyl Ketone	0.172	0.167	0.163	0.161	0.160	0.159
Methyl Propyl Ketone	0.174	0.169	0.166	0.164	0.163	0.163
Methyl Butyl Ketone	0.162	0.166	0.172	0.179	0.186	0.195
Acetylacetone	0.230	0.220	0.212	0.207	0.204	0.202
Methylene Chloride	0.076	0.074	0.074	0.073	0.073	0.073
Chloroform	0.061	0.063	0.064	0.066	0.068	0.070
1-Chloropentane	0.137	0.133	0.131	0.129	0.128	0.128
n-Butyronitrile	0.320	0.310	0.300	0.292	0.285	0.279
n-Valeronitrile	0.307	0.295	0.286	0.279	0.274	0.271

TABLE 21. Gibbs Free Energies of Solution $-\Delta\bar{G}_S$/kJ mol^{-1} for Listed Probe Solutes at Indicated Temperatures with Poly bd X-10LM R-45M

	$-\Delta\bar{G}_S$/kJ mol^{-1}					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	9.68	9.17	8.67	8.16	7.66	7.16
n-Hexane	12.38	11.81	11.24	10.67	10.10	9.54
n-Heptane	15.04	14.41	13.78	13.16	12.53	11.91
n-Octane	17.66	16.97	16.28	15.60	14.91	14.23
3-Methylpentane	11.89	11.35	10.82	10.29	9.76	9.23
2,3-Dimethyl-pentane	14.25	13.65	13.06	12.47	11.88	11.30
3-Methylhexane	14.35	13.75	13.14	12.54	11.94	11.35
3-Methylheptane	16.91	16.24	15.57	14.90	14.24	13.58
1-Hexene	12.38	11.81	11.24	10.67	10.10	9.54
1-Heptene	15.05	14.43	13.82	13.20	12.59	11.98
1-Octene	17.67	16.99	16.31	15.63	14.96	14.29
Benzene	15.52	14.94	14.37	13.80	13.23	12.67
Toluene	18.27	17.64	17.02	16.40	15.78	15.16
Ethylbenzene	20.48	19.83	19.18	18.53	17.89	17.24
o-Xylene	21.47	20.81	20.16	19.51	18.86	18.21
p-Xylene	20.81	20.15	19.50	18.85	18.20	17.55
Cyclohexane	14.49	13.95	13.40	12.86	12.32	11.79
Methylcyclo-hexane	15.95	15.38	14.81	14.24	13.67	13.11
Tetrahydrofuran	15.51	14.93	14.35	13.77	13.19	12.62
Thiophene	16.06	15.48	14.91	14.34	13.78	13.21
Acetone	11.97	11.43	10.89	10.35	9.82	9.28
Methyl Ethyl Ketone	14.45	13.88	13.31	12.74	12.18	11.62
Methyl Propyl Ketone	16.86	16.11	15.36	14.62	13.87	13.13
Methyl Butyl Ketone	19.36	18.67	17.98	17.29	16.61	15.92
Acetylacetone	19.29	18.64	17.99	17.34	16.69	16.05
Methylene Chloride	12.39	11.84	11.30	10.75	10.21	9.67
Chloroform	14.98	14.37	13.76	13.16	12.55	11.95
1-Chloropentane	17.35	16.70	16.05	15.40	14.75	14.11
n-Butyronitrile	16.54	15.90	15.26	14.63	14.00	13.37
n-Valeronitrile	19.17	18.47	17.77	17.07	16.38	15.69

TABLE 22. Gibbs Free Energies of Solution $-\bar{\Delta G}_S$/kJ mol^{-1} for Listed Probe Solutes at Indicated Temperatures with Poly bd X-14LM R-45M

	$-\bar{\Delta G}_S$/kJ mol^{-1}					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	9.51	9.17	8.49	7.99	7.48	6.98
n-Hexane	12.26	11.67	11.08	10.49	9.91	9.32
n-Heptane	14.93	14.29	13.66	13.03	12.41	11.78
n-Octane	17.58	16.89	16.20	15.51	14.82	14.14
3-Methylpentane	11.74	11.19	10.65	10.11	9.57	9.03
2,3-Dimethyl-pentane	14.04	13.45	12.86	12.27	11.69	11.10
3-Methylhexane	14.21	13.60	12.99	12.38	11.77	11.17
3-Methylheptane	16.78	16.11	15.44	14.77	14.10	13.43
1-Hexene	12.29	11.72	11.15	10.58	10.02	9.46
1-Heptene	14.94	14.32	13.69	13.08	12.46	11.84
1-Octene	17.58	16.89	16.21	15.53	14.85	14.17
Benzene	15.35	14.79	14.22	13.66	13.10	12.54
Toluene	18.17	17.53	16.90	16.28	15.65	15.03
Ethylbenzene	20.36	19.71	19.06	18.41	17.77	17.12
o-Xylene	21.39	20.72	20.06	19.40	18.75	18.09
p-Xylene	20.71	20.05	19.39	18.74	18.08	17.43
Cyclohexane	14.36	13.81	13.27	12.72	12.18	11.64
Methylcyclo-hexane	15.85	15.27	14.69	14.11	13.54	12.97
Tetrahydrofuran	15.31	14.71	14.11	13.51	12.92	12.33
Thiophene	15.93	15.34	14.77	14.19	13.62	13.04
Acetone	11.76	11.20	10.64	10.09	9.54	8.99
Methyl Ethyl Ketone	14.30	13.69	13.08	12.47	11.87	11.27
Methyl Propyl Ketone	16.58	15.92	15.27	14.61	13.96	13.31
Methyl Butyl Ketone	19.20	18.49	17.79	17.09	16.39	15.70
Acetylacetone	19.11	18.46	17.80	17.15	16.50	15.86
Methylene Chloride	12.21	11.66	11.12	10.58	10.04	9.51
Chloroform	14.80	14.19	13.59	12.99	12.39	11.79
1-Chloropentane	17.22	16.56	15.90	15.24	14.59	13.93
n-Butyronitrile	16.27	15.69	15.06	14.42	13.78	13.15
n-Valeronitrile	18.95	18.27	17.58	16.90	16.22	15.54

TABLE 23. Gibbs Free Energies of Solution $-\bar{A}G_S$/kJ mol^{-1} for Listed Probe Solutes at Indicated Temperatures with Poly bd X-20LM R-45M

	$-\bar{A}G_S$/kJ mol^{-1}					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	9.84	9.32	8.80	8.29	7.78	7.27
n-Hexane	12.56	11.97	11.39	10.82	10.24	9.67
n-Heptane	15.23	14.58	13.93	13.29	12.65	12.01
n-Octane	17.88	17.17	16.45	15.74	15.04	14.33
3-Methylpentane	12.04	11.48	10.92	10.37	9.82	9.27
2,3-Dimethyl-pentane	14.35	13.75	13.14	12.54	11.94	11.35
3-Methylhexane	14.52	13.89	13.27	12.65	12.03	11.42
3-Methylheptane	17.08	16.39	15.70	15.02	14.33	13.65
1-Hexene	12.55	11.98	11.41	10.84	10.28	9.71
1-Heptene	15.22	14.58	13.95	13.32	12.69	12.06
1-Octene	17.85	17.15	16.45	15.76	15.06	14.37
Benzene	15.54	14.97	14.40	13.84	13.28	12.72
Toluene	18.33	17.70	17.07	16.44	15.82	15.20
Ethylbenzene	20.56	19.90	19.24	18.58	17.92	17.27
o-Xylene	21.60	20.92	20.24	19.56	18.89	18.22
p-Xylene	20.93	20.26	19.58	18.91	18.23	17.56
Cyclohexane	14.67	14.10	13.54	12.98	12.43	11.87
Methylcyclo-hexane	16.15	15.55	14.96	14.37	13.78	13.19
Tetrahydrofuran	15.49	14.89	14.30	13.71	13.13	12.54
Thiophene	16.04	15.48	14.91	14.35	13.80	13.24
Acetone	11.89	11.35	10.83	10.31	9.80	9.28
Methyl Ethyl Ketone	14.41	13.81	13.22	12.62	12.03	11.45
Methyl Propyl Ketone	16.70	16.04	15.39	14.74	14.09	13.45
Methyl Butyl Ketone	19.32	18.62	17.91	17.21	16.51	15.82
Acetylacetone	19.17	18.52	17.87	17.23	16.58	15.94
Methylene Chloride	12.33	11.78	11.24	10.71	10.17	9.64
Chloroform	14.89	14.30	13.70	13.11	12.52	11.93
1-Chloropentane	17.39	16.73	16.08	15.43	14.78	14.13
n-Butyronitrile	16.35	15.72	15.09	14.47	13.84	13.22
n-Valeronitrile	18.96	18.29	17.61	16.94	16.26	15.60

TABLE 24. Replicate Measurement of Gibbs Free Energies of Solution $-\bar{A}G_S$/kJ mol^{-1} for Listed Probe Solutes at Indicated Temperatures with Poly bd X-20LM R-45M

	$-\bar{A}G_S$/kJ mol^{-1}					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	9.85	9.32	8.80	8.27	7.75	7.23
n-Hexane	12.57	11.97	11.38	10.79	10.20	9.62
n-Heptane	15.23	14.57	13.92	13.26	12.61	11.96
n-Octane	17.88	17.16	16.43	15.71	15.00	14.28
3-Methylpentane	12.04	11.48	10.92	10.37	9.81	9.26
2,3-Dimethyl-pentane	14.35	13.75	13.14	12.54	11.94	11.34
3-Methylhexane	14.51	13.88	13.26	12.64	12.02	11.40
3-Methylheptane	17.07	16.38	15.69	15.01	14.32	13.64
1-Hexene	12.58	11.99	11.41	10.84	10.26	9.69
1-Heptene	15.22	14.58	13.94	13.30	12.66	12.02
1-Octene	17.86	17.14	16.43	15.72	15.01	14.30
Benzene	15.51	14.94	14.38	13.81	13.25	12.69
Toluene	18.30	17.67	17.04	16.42	15.79	15.17
Ethylbenzene	20.48	19.83	19.18	18.54	17.90	17.26
o-Xylene	21.51	20.84	20.18	19.52	18.87	18.21
p-Xylene	20.86	20.19	19.53	18.87	18.21	17.55
Cyclohexane	14.66	14.10	13.54	12.98	12.42	11.86
Methylcyclo-hexane	16.14	15.55	14.95	14.36	13.77	13.18
Tetrahydrofuran	15.45	14.85	14.24	13.64	13.04	12.45
Thiophene	16.03	15.46	14.89	14.33	13.76	13.20
Acetone	11.81	11.27	10.72	10.17	9.63	9.09
Methyl Ethyl Ketone	14.37	13.77	13.17	12.57	11.97	11.37
Methyl Propyl Ketone	16.66	16.01	15.35	14.70	14.05	13.40
Methyl Butyl Ketone	19.30	18.59	17.88	17.17	16.47	15.77
Acetylacetone	19.11	18.47	17.83	17.20	16.57	15.94
Methylene Chloride	12.28	11.74	11.21	10.68	10.15	9.62
Chloroform	14.87	14.27	13.67	13.08	12.49	11.90
1-Chloropentane	17.37	16.71	16.06	15.41	14.76	14.12
n-Butyronitrile	16.25	15.64	15.03	14.41	13.81	13.20
n-Valeronitrile	18.94	18.26	17.58	16.90	16.23	15.56

TABLE 25. Gibbs Free Energies of Solution $-\bar{\Delta G}_S$/kJ mol^{-1} for Listed Probe Solutes at Indicated Temperatures with Poly bd X-25LM R-45M

	$-\bar{\Delta G}_S$/kJ mol^{-1}					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	9.73	9.20	8.66	8.13	7.60	7.08
n-Hexane	12.27	11.73	11.12	10.66	10.13	9.60
n-Heptane	15.11	14.47	13.83	13.19	12.56	11.93
n-Octane	17.77	17.07	16.36	15.66	14.95	14.26
3-Methylpentane	11.93	11.37	10.81	10.26	9.70	9.15
2,3-Dimethyl-pentane	14.23	13.63	13.04	12.44	11.85	11.26
3-Methylhexane	14.41	13.79	13.17	12.55	11.94	11.32
3-Methylheptane	16.97	16.29	15.61	14.93	14.25	13.58
1-Hexene	12.45	11.88	11.31	10.75	10.19	9.63
1-Heptene	15.12	14.49	13.86	13.23	12.60	11.98
1-Octene	17.75	17.06	16.36	15.67	14.98	14.30
Benzene	15.46	14.89	14.33	13.76	13.20	12.64
Toluene	18.26	17.63	17.00	16.37	15.75	15.13
Ethylbenzene	20.46	19.81	19.15	18.51	17.86	17.21
o-Xylene	21.48	20.86	20.15	19.50	18.84	18.18
p-Xylene	20.81	20.15	19.50	18.84	18.18	17.53
Cyclohexane	14.55	13.99	13.44	12.88	12.33	11.78
Methylcyclo-hexane	16.04	15.45	14.86	14.28	13.69	13.11
Tetrahydrofuran	15.30	14.71	14.11	13.52	12.93	12.34
Thiophene	16.01	15.43	14.86	14.29	13.72	13.15
Acetone	11.79	11.21	10.64	10.06	9.49	8.92
Methyl Ethyl Ketone	14.31	13.69	13.07	12.45	11.83	11.22
Methyl Propyl Ketone	16.60	15.93	15.26	14.59	13.93	13.27
Methyl Butyl Ketone	19.22	18.50	17.78	17.06	16.35	15.64
Acetylacetone	19.12	18.45	17.78	17.12	16.45	15.79
Methylene Chloride	12.26	11.71	11.17	10.63	10.10	9.56
Chloroform	14.84	14.24	13.64	13.04	12.44	11.85
1-Chloropentane	17.28	16.64	15.99	15.35	14.71	14.08
n-Butyronitrile	16.26	15.63	14.99	14.36	13.73	13.10
n-Valeronitrile	18.88	18.19	17.51	16.83	16.15	15.47

TABLE 26. Gibbs Free Energies of Solution $-\Delta\bar{G}_S$/kJ mol^{-1} for Listed Probe Solutes at Indicated Temperatures with Poly bd X-120HM R-45M

	$-\Delta G_S$/kJ mol^{-1}					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	9.73	9.13	8.52	7.93	7.33	6.73
n-Hexane	12.48	11.81	11.14	10.47	9.81	9.15
n-Heptane	15.15	14.42	13.69	12.97	12.24	11.52
n-Octane	17.79	16.70	16.21	15.42	14.64	13.86
3-Methylpentane	11.85	11.29	10.74	10.20	9.65	9.11
2,3-Dimethyl-pentane	14.16	13.57	12.98	12.39	11.80	11.22
3-Methylhexane	14.32	13.71	13.10	12.50	11.89	11.29
3-Methylheptane	16.88	16.21	15.54	14.87	14.20	13.54
1-Hexene	12.50	11.83	11.16	10.50	9.84	9.18
1-Heptene	15.05	14.40	13.76	13.11	12.48	11.84
1-Octene	17.69	16.98	16.26	15.55	14.84	14.14
Benzene	15.41	14.82	14.24	13.67	13.09	12.52
Toluene	18.20	17.56	16.91	16.28	15.64	15.00
Ethylbenzene	20.39	19.73	19.06	18.41	17.75	17.09
o-Xylene	21.47	20.78	20.09	19.41	18.73	18.05
p-Xylene	20.80	20.12	19.43	18.75	18.07	17.39
Cyclohexane	14.60	13.95	13.30	12.66	12.01	11.37
Methylcyclo-hexane	16.07	15.40	14.72	14.05	13.38	12.71
Tetrahydrofuran	15.01	14.39	13.78	13.17	12.56	11.95
Thiophene	15.97	15.37	14.78	14.19	13.60	13.01
Acetone	11.63	11.00	10.36	9.74	9.11	8.49
Methyl Ethyl Ketone	14.05	13.39	12.74	12.08	11.43	10.78
Methyl Propyl Ketone	16.32	15.62	14.92	14.22	13.52	12.82
Methyl Butyl Ketone	19.23	18.33	17.43	16.53	15.64	14.75
Acetylacetone	18.93	18.22	17.51	16.80	16.10	15.39
Methylene Chloride	12.23	11.65	11.07	10.50	9.93	9.36
Chloroform	14.80	14.17	13.54	12.90	12.28	11.65
1-Chloropentane	17.24	16.58	15.91	15.25	14.60	13.94
n-Butyronitrile	16.10	15.41	14.72	14.04	13.35	12.67
n-Valeronitrile	18.77	18.01	17.23	16.52	15.78	15.03

TABLE 27. Entropies of Solution $\Delta\bar{S}_S$/e.u. for Listed Probe Solutes at Indicated Temperatures with Poly bd X-10LM R-45M

	$\Delta\bar{S}_S$/e.u.					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	38.15	37.95	37.75	37.55	37.35	37.20
n-Hexane	44.65	44.45	44.25	44.05	43.85	43.65
n-Heptane	50.25	50.05	49.85	49.65	49.45	49.25
n-Octane	56.35	56.10	55.90	55.70	55.55	55.35
3-Methylpentane	40.95	40.75	40.55	40.35	40.15	39.95
2,3-Dimethyl-pentane	46.75	46.50	46.30	46.10	45.90	45.75
3-Methylhexane	47.90	47.70	47.50	47.30	47.10	46.95
3-Methylheptane	54.30	54.10	53.90	53.70	53.50	53.35
1-Hexene	44.65	44.45	44.25	44.05	43.85	43.65
1-Heptene	49.25	49.00	48.80	48.60	48.45	48.25
1-Octene	55.30	55.10	54.90	54.70	54.50	54.35
Benzene	44.70	44.50	44.30	44.10	43.90	43.70
Toluene	49.80	49.60	49.40	49.20	49.00	48.85
Ethylbenzene	52.55	52.35	52.15	51.95	51.75	51.55
o-Xylene	53.00	52.75	52.55	52.35	52.20	52.00
p-Xylene	53.00	52.80	52.55	52.35	52.20	52.00
Cyclohexane	41.85	41.65	41.45	41.25	41.05	40.90
Methylcyclo-hexane	44.65	44.40	44.20	44.00	43.85	43.65
Tetrahydrofuran	45.55	45.35	45.15	44.95	44.75	44.60
Thiophene	44.65	44.45	44.25	44.05	43.85	43.70
Acetone	41.60	41.35	41.15	41.95	40.75	40.60
Methyl Ethyl Ketone	44.30	44.10	43.90	43.70	43.50	43.35
Methyl Propyl Ketone	62.55	62.30	62.10	61.90	61.75	61.55
Methyl Butyl Ketone	56.40	56.20	56.00	55.80	55.60	55.45
Acetylacetone	52.60	52.40	52.20	52.00	51.80	51.65
Methylene Chloride	42.25	42.05	41.85	41.65	41.45	41.25
Chloroform	48.35	48.10	47.90	47.70	47.55	47.35
1-Chloropentane	52.65	52.45	52.25	52.05	51.85	51.70
n-Butyronitrile	51.10	50.90	50.70	50.50	50.30	50.10
n-Valeronitrile	57.35	57.15	56.95	56.75	56.55	56.35

TABLE 28. Entropies of Solution $\bar{A}S_S$/e.u. for Listed Probe Solutes at Indicated Temperatures with Poly bd X-14LM R-45M

	$\bar{A}S_S$/e.u.					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	38.30	38.10	37.90	37.70	37.50	37.30
n-Hexane	46.50	46.30	46.10	45.90	45.70	45.50
n-Heptane	50.65	50.45	50.25	50.05	49.85	49.65
n-Octane	56.65	56.45	56.25	56.05	55.85	55.65
3-Methylpentane	42.00	41.80	41.60	41.40	41.20	41.00
2,3-Dimethyl-pentane	46.45	46.20	46.00	45.80	45.60	45.45
3-Methylhexane	48.50	48.30	48.10	47.90	47.70	47.55
3-Methylheptane	54.80	54.60	54.40	54.20	54.00	53.85
1-Hexene	44.30	44.05	43.85	43.65	43.45	43.30
1-Heptene	49.80	49.60	49.40	49.20	49.00	49.85
1-Octene	55.90	55.70	55.50	55.30	55.10	54.90
Benzene	43.90	43.70	43.50	43.30	43.10	42.90
Toluene	50.50	50.30	50.10	49.90	49.70	49.50
Ethylbenzene	52.55	52.30	52.10	51.90	51.70	51.55
o-Xylene	53.70	53.50	53.30	53.10	52.90	52.70
p-Xylene	53.30	53.10	52.90	52.70	52.50	52.35
Cyclohexane	42.35	42.10	41.90	41.70	41.50	41.35
Methylcyclo-hexane	45.35	45.15	44.95	44.75	44.55	44.40
Tetrahydrofuran	47.25	47.05	46.85	46.65	46.45	46.25
Thiophene	45.40	45.20	45.00	44.75	44.55	44.40
Acetone	43.20	43.00	42.80	42.60	42.40	42.25
Methyl Ethyl Ketone	48.30	48.10	47.90	47.70	47.50	47.30
Methyl Propyl Ketone	53.10	52.90	52.70	52.50	52.30	52.10
Methyl Butyl Ketone	57.80	57.55	57.35	57.15	56.95	56.80
Acetylacetone	52.80	52.60	52.40	52.20	52.00	51.85
Methylene Chloride	41.75	41.55	41.35	41.15	40.95	40.75
Chloroform	47.90	47.70	47.50	47.30	47.10	46.90
1-Chloropentane	53.45	53.25	53.05	52.85	52.65	52.45
n-Butyronitrile	50.45	50.10	49.90	49.75	49.55	49.40
n-Valeronitrile	56.05	55.80	55.60	55.40	55.25	55.05

TABLE 29. Entropies of Solution $\Delta\bar{S}_S$/e.u. for Listed Probe Solutes at Indicated Temperatures with Poly bd X-20LM R-45M

	ΔS_S/e.u.					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	39.10	38.90	38.70	38.50	38.30	38.10
n-Hexane	45.50	45.30	45.10	44.90	44.70	44.50
n-Heptane	52.10	51.90	51.70	51.50	51.30	51.10
n-Octane	58.75	58.50	58.30	58.10	57.95	57.75
3-Methylpentane	42.95	42.75	42.55	42.35	42.15	42.00
2,3-Dimethyl-pentane	47.80	47.60	47.40	47.20	47.00	46.80
3-Methylhexane	49.80	49.60	49.35	49.15	49.00	48.80
3-Methylheptane	56.30	56.10	55.90	55.70	55.50	55.30
1-Hexene	44.45	44.25	44.00	43.80	43.65	43.45
1-Heptene	50.80	50.60	50.40	50.20	50.00	49.80
1-Octene	57.25	57.05	56.80	56.60	56.45	56.25
Benzene	44.10	43.90	43.65	43.45	43.30	43.10
Toluene	50.20	50.00	49.75	49.55	49.40	49.20
Ethylbenzene	53.55	53.35	53.15	52.95	52.75	52.55
o-Xylene	55.45	55.25	55.05	54.85	54.65	54.45
p-Xylene	55.10	54.90	54.65	54.45	54.30	54.10
Cyclohexane	43.50	43.30	43.10	42.90	42.70	42.50
Methylcyclo-hexane	46.85	46.60	46.40	46.20	46.05	45.85
Tetrahydrofuran	46.60	46.40	46.20	46.00	45.80	45.60
Thiophene	43.80	43.55	43.35	43.15	42.95	42.80
Acetone	39.60	39.40	39.20	39.00	38.80	38.60
Methyl Ethyl Ketone	46.90	46.70	46.45	46.25	46.10	45.90
Methyl Propyl Ketone	52.65	52.45	52.20	52.00	51.85	51.65
Methyl Butyl Ketone	57.75	57.55	57.35	57.15	56.95	56.75
Acetylacetone	52.30	52.10	51.90	51.70	51.50	51.30
Methylene Chloride	41.45	41.25	41.05	40.85	40.65	40.45
Chloroform	47.05	46.85	46.60	46.45	46.25	46.05
1-Chloropentane	52.75	52.55	52.35	52.15	51.95	51.80
n-Butyronitrile	50.30	50.05	49.85	49.65	49.45	49.30
n-Valeronitrile	55.05	54.80	54.60	54.40	54.25	54.05

TABLE 30. Replicate Measurement of Entropies of Solution $\Delta\bar{S}_S$/e.u. for Listed Probe Solutes at Indicated Temperatures with Poly bd X-20LM R-45M

	$\Delta\bar{S}_S$/e.u.					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	40.15	39.95	39.75	39.55	39.35	39.15
n-Hexane	46.75	46.55	46.30	46.10	45.95	45.75
n-Heptane	53.10	52.90	52.70	52.50	52.30	52.10
n-Octane	59.70	59.45	59.25	59.05	58.85	58.70
3-Methylpentane	43.25	43.00	42.80	42.60	42.40	42.25
2,3-Dimethyl-pentane	47.90	47.65	47.45	47.25	47.05	46.90
3-Methylhexane	49.80	49.60	49.35	49.20	49.00	48.80
3-Methylheptane	56.20	55.95	55.75	55.55	55.35	55.20
1-Hexene	45.45	45.25	45.00	44.85	44.65	44.45
1-Heptene	51.75	51.55	51.35	51.15	50.95	50.75
1-Octene	58.80	58.60	58.40	58.20	58.00	57.80
Benzene	44.05	43.85	43.60	43.40	43.25	43.05
Toluene	50.25	50.00	49.80	49.60	49.45	49.25
Ethylbenzene	52.15	51.95	51.75	51.55	51.35	51.15
o-Xylene	53.60	53.40	53.20	53.00	52.80	52.60
p-Xylene	53.90	53.65	53.45	53.25	53.05	52.90
Cyclohexane	43.75	43.50	43.30	43.10	42.95	42.75
Methylcyclo-hexane	46.90	46.70	46.50	46.30	46.10	45.90
Tetrahydrofuran	47.80	47.60	47.40	47.20	47.00	46.80
Thiophene	44.30	44.10	43.90	43.70	43.50	43.30
Acetone	42.10	41.90	41.70	41.50	41.30	41.15
Methyl Ethyl Ketone	47.65	47.45	47.20	47.00	46.85	46.65
Methyl Propyl Ketone	52.85	52.60	52.40	52.20	52.00	51.85
Methyl Butyl Ketone	58.25	58.05	57.85	57.65	57.45	57.25
Acetylacetone	51.10	50.90	50.65	50.45	50.30	50.10
Methylene Chloride	40.80	40.60	40.40	40.20	40.00	39.80
Chloroform	46.90	46.70	46.50	46.30	46.10	45.90
1-Chloropentane	52.70	52.50	52.30	52.10	51.90	51.70
n-Butyronitrile	48.80	48.55	48.35	48.15	47.95	47.80
n-Valeronitrile	55.35	55.15	54.95	54.75	54.55	54.35

TABLE 31. Entropies of Solution $\Delta\bar{S}_S$/e.u. for Listed Probe Solutes at Indicated Temperatures with Poly bd X-25LM R-45M

	ΔS_S/e.u.					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	40.80	40.60	40.35	40.15	40.00	39.80
n-Hexane	40.95	40.75	40.50	40.30	40.15	39.95
n-Heptane	51.40	51.20	51.00	50.80	50.60	50.40
n-Octane	58.00	57.75	57.55	57.35	57.15	57.00
3-Methylpentane	43.10	42.90	42.70	42.50	42.30	42.10
2,3-Dimethyl-pentane	47.20	47.00	46.75	46.55	46.40	46.20
3-Methylhexane	49.30	49.10	48.90	48.70	48.50	48.30
3-Methylheptane	55.30	55.10	54.90	54.70	54.50	54.30
1-Hexene	44.05	43.80	43.60	43.40	43.20	43.05
1-Heptene	50.30	50.10	49.90	49.70	49.50	49.30
1-Octene	56.70	56.50	56.30	56.10	55.90	55.70
Benzene	44.15	43.90	43.70	43.50	43.30	43.15
Toluene	50.25	50.05	49.85	49.65	49.45	49.25
Ethylbenzene	52.55	52.35	52.15	51.95	51.75	51.55
o-Xylene	54.10	53.75	53.65	53.45	53.25	53.05
p-Xylene	53.35	53.15	52.95	52.75	52.55	52.35
Cyclohexane	43.20	43.00	42.80	42.60	42.40	42.20
Methylcyclo-hexane	46.15	45.95	45.75	45.55	45.35	45.15
Tetrahydrofuran	46.95	46.70	46.50	46.30	46.10	45.95
Thiophene	44.85	44.65	44.45	44.25	44.05	43.85
Acetone	45.10	44.90	44.70	44.50	44.30	44.10
Methyl Ethyl Ketone	49.50	49.30	49.10	48.90	48.70	48.50
Methyl Propyl Ketone	54.30	54.05	53.85	53.65	53.45	53.30
Methyl Butyl Ketone	59.15	58.90	58.70	58.50	58.30	58.15
Acetylacetone	54.20	54.00	53.80	53.60	53.40	53.20
Methylene Chloride	41.45	41.25	41.05	40.85	40.65	40.45
Chloroform	47.55	47.35	47.15	46.95	46.75	46.55
1-Chloropentane	51.70	51.50	51.30	51.10	50.90	50.70
n-Butyronitrile	50.90	50.65	50.45	50.25	50.05	49.90
n-Valeronitrile	55.95	55.75	55.55	55.35	55.15	54.95

TABLE 32. Entropies of Solution $\Delta\bar{S}_S$/e.u. for Listed Probe Solutes at Indicated Temperatures with Poly bd X-120HM R-45M

	$\Delta\bar{S}_S$/e.u.					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	47.65	47.45	47.25	47.05	46.85	46.65
n-Hexane	54.30	54.10	53.90	53.70	53.50	53.30
n-Heptane	60.40	60.15	59.95	59.75	59.55	59.40
n-Octane	66.35	66.10	65.90	65.70	65.50	65.35
3-Methylpentane	42.50	42.25	42.05	41.85	41.65	41.50
2,3-Dimethyl-pentane	46.45	46.25	46.05	45.85	45.65	45.45
3-Methylhexane	48.45	48.25	48.05	47.85	47.65	47.45
3-Methylheptane	54.70	54.50	54.30	54.10	53.90	53.70
1-Hexene	54.10	53.90	53.70	53.50	53.30	53.10
1-Heptene	51.85	51.65	51.45	51.25	51.05	50.85
1-Octene	58.75	58.55	58.35	58.15	57.95	57.80
Benzene	45.45	45.25	45.00	44.85	44.65	44.45
Toluene	51.65	51.45	51.25	51.05	50.85	50.65
Ethylbenzene	53.60	53.40	53.20	53.00	52.80	52.65
o-Xylene	56.10	55.90	55.65	55.45	55.30	55.10
p-Xylene	55.95	55.70	55.50	55.30	55.15	54.95
Cyclohexane	52.25	52.05	51.85	51.65	51.45	51.25
Methylcyclo-hexane	55.05	54.85	54.65	54.45	54.25	54.05
Tetrahydrofuran	48.85	48.65	48.40	48.20	48.05	47.85
Thiophene	46.85	46.65	46.45	46.25	46.05	45.85
Acetone	50.60	50.40	50.20	50.00	49.80	49.60
Methyl Ethyl Ketone	53.10	52.90	52.70	52.50	52.30	52.10
Methyl Propyl Ketone	57.65	57.45	57.25	57.05	56.85	56.65
Methyl Butyl Ketone	77.20	77.00	76.80	76.60	76.40	76.20
Acetylacetone	58.55	58.35	58.15	57.95	57.75	57.55
Methylene Chloride	45.20	45.00	44.80	44.60	44.40	44.20
Chloroform	50.65	50.45	50.25	50.05	49.85	49.65
1-Chloropentane	53.80	53.60	53.40	53.20	53.00	52.80
n-Butyronitrile	56.30	56.10	55.90	55.70	55.50	55.30
n-Valeronitrile	62.35	62.15	61.95	61.75	61.55	61.35

TABLE 33. Enthalpies of Solution $-\Delta\bar{H}_S$/kJ mol^{-1} for Listed Probe Solutes with Indicated Lots of Poly bd R-45M

	$-\Delta H_S$/kJ mol^{-1}					
	10LM	14LM	20LM/1	20LM/2	25LM	120HM
n-Pentane	25.20	25.08	25.66	25.99	26.08	28.12
n-Hexane	29.87	30.31	30.32	30.71	28.66	32.88
n-Heptane	34.22	34.23	34.98	35.30	34.68	37.40
n-Octane	38.69	38.71	39.65	39.94	39.33	41.84
3-Methylpentane	28.26	28.43	29.03	29.11	28.98	28.66
2,3-Dimethyl-pentane	32.36	32.07	32.81	32.83	32.52	32.18
3-Methylhexane	32.83	32.87	33.58	33.57	33.34	32.95
3-Methylheptane	37.33	37.36	38.12	38.07	37.72	37.41
1-Hexene	29.87	29.66	29.99	30.32	29.78	32.84
1-Heptene	33.93	34.00	34.58	34.88	34.35	34.71
1-Octene	38.39	38.47	39.17	39.65	38.92	39.45
Benzene	33.02	32.61	32.87	32.83	32.82	33.12
Toluene	37.32	37.43	37.51	37.49	37.48	37.80
Ethylbenzene	40.37	40.24	40.76	40.26	40.38	40.58
o-Xylene	41.49	41.62	42.38	41.73	41.86	42.41
p-Xylene	40.83	40.83	41.60	41.16	40.97	41.70
Cyclohexane	31.14	31.15	31.82	31.89	31.63	34.38
Methylcyclo-hexane	33.44	33.55	34.31	34.33	34.01	36.70
Tetrahydrofuran	33.28	33.59	33.58	33.91	33.51	33.75
Thiophene	33.56	33.63	33.28	33.43	33.59	34.12
Acetone	28.53	28.81	27.85	28.55	29.45	30.91
Methyl Ethyl Ketone	31.83	32.90	32.59	32.78	33.30	34.09
Methyl Propyl Ketone	39.77	36.63	36.62	36.64	37.04	37.74
Methyl Butyl Ketone	40.41	40.67	40.80	40.92	41.12	46.57
Acetylacetone	39.19	39.08	39.00	38.56	39.54	40.62
Methylene Chloride	29.16	28.82	28.86	28.61	28.81	29.87
Chloroform	33.58	33.28	33.12	33.05	33.24	34.10
1-Chloropentane	37.27	37.38	37.35	37.31	36.94	37.49
n-Butyronitrile	35.98	35.52	35.56	35.01	35.67	37.11
n-Valeronitrile	40.51	39.90	39.61	39.69	39.83	41.61

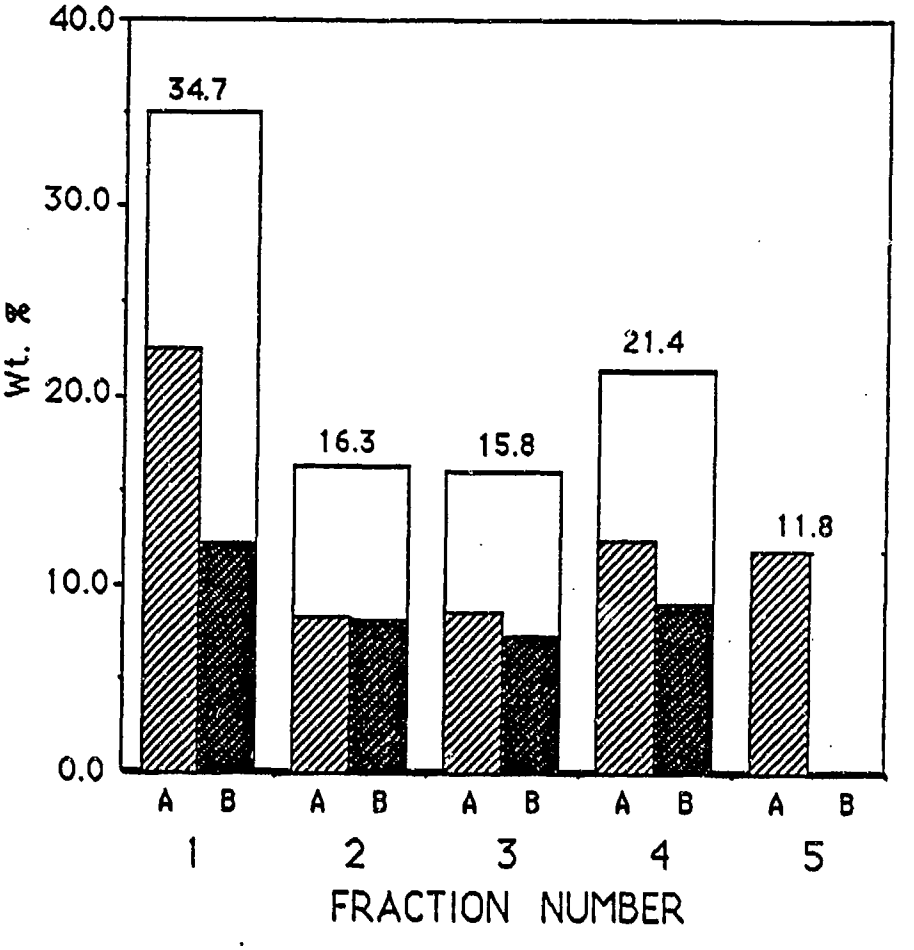

FIGURE 4. Plot of amounts extracted from ARCO X-25LM by solvent solution with IPA + benzene as a function of fraction number.

Specific Retention Volumes with Fractionated R-45M

The gas-chromatographic specific retention volumes, and van't Hoff slopes, intercepts, and least-squares correlation coefficients of all probe-solutes with each of the fractions of X-25LM at 30-80°C, are presented in Tables 34-51.

Data Interpretation

At this point the specific retention volumes, $V_g^o/cm^3\ g^{-1}$, and retention indices, I, of a bank of roughly 30 probe-solutes had been determined with bulk and fractionated polybutadiene and hydroxy-terminated polybutadiene R-45M, including several well-characterized lots of the latter. However, and while some general trends could be identified in the data, no firm correlations had thus far been drawn between the retentions of the probe-solutes and the properties (particularly the molecular weights) of R-45M stationary phases.

We therefore evaluated at this point the retentions of representative probe-solutes as a function of the number-average molecular weights, M_n, of the ARCO lots of R-45M. In doing so, a new technique was employed for screening for compounds whose molar specific retention volumes, $V_g^{o\prime}/cm^3\ mol^{-1}$, reflect the stationary phase molar mass. Modes of regression of the conventional-form specific retention volumes, $V_g^o/cm^3\ g^{-1}$, of promising solutes were then regressed directly against M_n as well as its inverse. Linear nomographs resulting from the latter (least-squares correlation coefficients r of in excess of 0.9999) were then used to calculate the number-average molecular weights of several fractions of R-45M that were obtained by solvent extraction. The considerable success of the technique, coupled with the ease with which it was implemented, indicated that inverse gas chromatography can also be applied to other prepolymer species as well.

Molar Specific Retention Volumes. The $V_g^{o\prime}$ of the representative solutes n-hexane, 3-methylhexane, 1-hexene, cyclohexane, benzene, tetrahydrofuran, 1-chloropentane, thiophene, acetone, chloroform, and valeronitrile with the ARCO lots of R-45M at 30° and 50°C are provided in Table 52. A quick assessment of the extent to which the solute retentions reflect the stationary phase molecular weight can be made by glancing through the molar specific retention volumes obtained with 14LM (1420 Da) and 20LM (1350 Da): since the molecular weight of 20LM is less than 14LM, the molar retentions of the solutes should be larger with the latter stationary phase. The data for the first seven solutes, Table 52.A, fail to exhibit this trend, and all of the $V_g^{o\prime}$ with 20LM are higher than those with 14LM. These compounds (including, somewhat surprisingly, the alkanes) must therefore be said to be poor probes of the solvent molecular weight. In contrast, the last four solutes, Table 52.B, precisely reflect the M_n of the stationary phases. Moreover, thiophene and valeronitrile appear to be particularly sensitive to M_n; for example, the molar retentions of the latter compound increase from 2095 to 5683 $cm^3\ mol^{-1}$ as the stationary phase molecular weight rises from 1040 to 3335 Da. The molar specific retention volume form of data reduction thus provides a quick method of screening for solutes that are potentially useful, as well as eliminating those that fail to conform, as molecular-weight probes.

Figures 5-8 present the regressions of the molar specific retention volumes of the solutes of Table 52.B against the number-average molecular weights of the ARCO lots of R-45M, where all appear to be quite linear. The regressions also suggest that the solute retentions are insensitive to functionality differences in the prepolymers (cf. Table 1).

TABLE 34. Smoothed (van't Hoff) Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ for Listed Probe Solutes at Indicated Temperatures with Fraction 1A of X-25LM R-45M

	$V_g^o/cm^3\ g^{-1}$					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	46.22	34.15	25.71	19.69	15.31	12.08
n-Hexane	135.2	94.35	67.33	49.02	36.36	27.43
n-Heptane	388.8	255.8	172.8	119.5	84.39	60.81
n-Octane	1105.	686.2	438.7	288.2	194.0	133.5
3-Methylpentane	111.9	78.91	56.84	41.76	31.23	23.75
2,3-Dimethyl-pentane	277.2	187.5	130.0	92.09	66.57	49.02
3-Methylhexane	295.5	197.9	135.9	95.41	68.40	49.97
3-Methylheptane	812.2	513.7	334.2	223.2	152.6	106.6
1-Hexene	138.5	96.90	69.33	50.61	37.63	28.45
1-Heptene	392.8	259.4	175.8	121.9	86.41	62.44
1-Octene	1108.	691.4	444.1	292.9	197.9	136.8
Benzene	464.1	313.7	217.2	153.7	111.0	81.68
Toluene	1395.	887.9	581.2	390.3	268.2	188.3
Ethylbenzene	3364.	2058.	1298.	841.5	559.5	380.7
o-Xylene	5057.	3038.	1884.	1202.	787.4	528.3
p-Xylene	3924.	2372.	1479.	948.9	624.7	421.1
Cyclohexane	315.6	216.1	151.5	108.5	79.25	58.92
Methylcyclo-hexane	565.7	375.6	255.7	178.2	126.8	92.01
Tetrahydrofuran	502.5	335.1	229.1	160.2	114.4	83.30
Thiophene	577.3	387.3	266.3	187.3	134.5	98.36
Acetone	124.8	89.26	65.19	48.52	36.73	28.26
Methyl Ethyl Ketone	334.6	226.7	157.4	111.7	80.87	59.62
Methyl Propyl Ketone	819.0	528.5	350.5	238.2	165.6	117.5
Methyl Butyl Ketone	2299.	1407.	887.0	575.1	382.4	260.2
Acetylacetone	2141.	1345.	869.5	577.0	392.2	272.5
Methylene Chloride	134.4	95.81	69.78	51.79	39.11	30.01
Chloroform	373.3	251.9	174.1	123.1	88.76	65.21
1-Chloropentane	957.8	612.9	403.2	272.0	187.7	132.3
n-Butyronitrile	719.0	473.1	319.5	220.9	156.0	112.4
n-Valeronitrile	2020.	1261.	810.4	534.9	361.7	250.0
1,2-Dimethoxy-ethane	708.3	455.4	300.9	203.9	141.3	99.95

TABLE 35. Slopes m, Intercepts b, and Linear Regression Correlation Coefficients r for van't Hoff Plots of Ln V_g^o of Listed Probe-Solutes of Table 34 Against $10^3\ T^{-1}$ with Fraction 1A of X-25LM R-45M

Probe Solute	m	- b	r
n-Pentane	2.873	5.643	0.9997_5
n-Hexane	3.415	6.360	0.9998_3
n-Heptane	3.973	7.141	0.9998_1
n-Octane	4.526	7.921	0.9998_6
3-Methylpentane	3.320	6.232	0.9998_7
2,3-Dimethylpentane	3.710	6.612	0.9998_6
3-Methylhexane	3.805	6.864	0.9998_4
3-Methylheptane	4.349	7.645	0.9998_4
1-Hexene	3.388	6.245	0.9999_4
1-Heptene	3.938	7.017	0.9998_4
1-Octene	4.480	7.768	0.9998_4
Benzene	3.720	6.131	0.9998_4
Toluene	4.288	6.904	0.9998_8
Ethylbenzene	4.665	7.268	0.9999_0
o-Xylene	4.837	7.427	0.9999_2
p-Xylene	4.779	7.489	0.9997_9
Cyclohexane	3.594	6.100	0.9998_8
Methylcyclohexane	3.889	6.489	0.9998_6
Tetrahydrofuran	3.848	6.474	0.9998_8
Thiophene	3.789	6.142	0.9998_9
Acetone	3.180	5.664	0.9997_2
Methyl Ethyl Ketone	3.693	6.369	0.9999_9
Methyl Propyl Ketone	4.158	7.007	0.9999_6
Methyl Butyl Ketone	4.665	7.648	0.9999_5
Acetylacetone	4.414	6.891	0.9999_7
Methylene Chloride	3.209	5.686	0.9998_8
Chloroform	3.736	6.401	0.9998_9
1-Chloropentane	4.238	7.114	0.9998_9
n-Butyronitrile	3.974	6.530	0.9999_7
n-Valeronitrile	4.473	7.144	0.9999_8
1,2-Dimethoxyethane	4.193	7.268	0.9999_7

TABLE 36. Replicate Smoothed (van't Hoff) Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ for Listed Probe Solutes at Indicated Temperatures with Fraction 1B of X-25LM R-45M

	$V_g^o/cm^3\ g^{-1}$					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	47.12	34.78	26.16	20.01	15.55	12.26
n-Hexane	138.5	96.57	68.86	50.11	37.15	28.01
n-Heptane	398.7	262.5	177.4	122.7	86.71	62.50
n-Octane	1131.	703.5	450.7	296.5	199.9	137.8
3-Methylpentane	113.0	80.13	58.03	42.85	32.20	24.60
2,3-Dimethyl-pentane	282.3	191.1	132.6	94.02	68.02	50.12
3-Methylhexane	300.6	201.6	138.5	97.35	69.85	51.06
3-Methylheptane	825.4	523.3	341.2	228.3	156.4	109.4
1-Hexene	140.9	98.12	69.87	50.78	37.60	28.32
1-Heptene	400.7	264.9	179.7	124.8	88.49	63.99
1-Octene	1134.	707.6	454.7	300.1	202.9	140.3
Benzene	466.7	315.5	218.6	154.8	111.8	82.28
Toluene	1409.	896.9	587.2	394.4	271.1	190.3
Ethylbenzene	3408.	2084.	1314.	851.6	566.1	385.1
o-Xylene	5124.	3078.	1908.	1217.	797.1	534.7
p-Xylene	3976.	2401.	1496.	958.8	630.7	424.8
Cyclohexane	321.4	220.3	154.6	110.8	80.95	60.22
Methylcyclo-hexane	577.8	384.1	261.9	182.7	130.2	94.54
Tetrahydrofuran	480.6	321.8	220.8	155.0	111.1	81.12
Thiophene	580.3	389.0	267.2	187.8	134.7	98.47
Acetone	120.4	85.83	62.46	46.33	34.97	26.82
Methyl Ethyl Ketone	322.1	218.1	151.3	107.2	77.57	57.15
Methyl Propyl Ketone	792.7	511.0	338.5	229.8	159.6	113.1
Methyl Butyl Ketone	2213.	1357.	858.1	557.6	371.5	253.3
Acetylacetone	2115.	1318.	845.6	557.1	376.1	259.6
Methylene Chloride	134.4	95.37	69.15	51.11	38.45	29.40
Chloroform	373.5	251.0	172.9	121.8	87.53	64.11
1-Chloropentane	965.7	617.1	405.4	273.1	188.3	132.6
n-Butyronitrile	699.4	457.2	306.8	210.9	148.2	106.2
n-Valeronitrile	1971.	1222.	780.5	512.0	344.3	236.8
1,2-Dimethoxy-ethane	685.6	439.9	290.1	196.2	135.7	95.87

TABLE 37. Slopes m, Intercepts b, and Linear Regression Correlation Coefficients r for van't Hoff Plots of Ln V_g^o of Listed Probe-Solutes of Table 36 Against 10^3 T^{-1} with Fraction 1B of X-25LM R-45M

Probe Solute	m	- b	r
n-Pentane	2.882	5.657	0.9998_5
n-Hexane	3.422	6.358	0.9998_4
n-Heptane	3.968	7.101	0.9998_0
n-Octane	4.506	7.834	0.9998_6
3-Methylpentane	3.266	6.044	0.9998_3
2,3-Dimethylpentane	3.701	6.566	0.9998_8
3-Methylhexane	3.796	6.816	0.9999_1
3-Methylheptane	4.327	7.556	0.9999_2
1-Hexene	3.436	6.386	0.9999_1
1-Heptene	3.928	6.964	0.9998_2
1-Octene	4.475	7.727	0.9998_4
Benzene	3.716	6.113	0.9998_9
Toluene	4.286	6.887	0.9999_0
Ethylbenzene	4.668	7.265	0.9999_7
o-Xylene	4.839	7.421	0.9999_9
p-Xylene	4.788	7.508	0.9999_9
Cyclohexane	3.586	6.056	0.9999_6
Methylcyclohexane	3.876	6.426	0.9999_3
Tetrahydrofuran	3.810	6.391	0.9999_4
Thiophene	3.798	6.165	0.9999_5
Acetone	3.216	5.816	0.9999_6
Methyl Ethyl Ketone	3.702	6.437	0.9999_7
Methyl Propyl Ketone	4.169	7.076	0.9999_8
Methyl Butyl Ketone	4.641	7.607	0.9999_2
Acetylacetone	4.492	7.160	0.9999_8
Methylene Chloride	3.254	5.833	0.9999_4
Chloroform	3.773	6.523	0.9999_3
1-Chloropentane	4.252	7.153	0.9999_2
n-Butyronitrile	4.036	6.762	0.9999_6
n-Valeronitrile	4.537	7.380	0.9999_9
1,2-Dimethoxy-ethane	4.212	7.365	0.9999_4

TABLE 38. Smoothed (van't Hoff) Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ for Listed Probe Solutes at Indicated Temperatures with Fraction 2A of X-25LM R-45M

	$V_g^o/cm^3\ g^{-1}$					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	45.83	34.08	25.81	19.88	15.54	12.32
n-Hexane	135.9	95.13	68.09	49.72	36.98	27.97
n-Heptane	391.3	258.7	175.5	121.9	86.42	62.50
n-Octane	1113.	695.1	447.2	295.4	199.9	138.3
3-Methylpentane	110.1	78.56	57.22	42.48	32.09	24.63
2,3-Dimethyl-pentane	276.8	188.1	130.9	93.07	67.51	49.87
3-Methylhexane	294.9	198.7	137.2	96.82	69.75	51.19
3-Methylheptane	812.4	517.5	339.0	227.7	156.6	110.0
1-Hexene	136.8	95.80	68.58	50.09	37.27	28.19
1-Heptene	392.6	260.4	177.2	123.4	87.72	63.60
1-Octene	1112.	696.5	449.0	297.2	201.6	139.7
Benzene	457.4	308.9	213.8	151.2	109.2	80.26
Toluene	1383.	880.3	576.3	387.0	266.0	186.7
Ethylbenzene	3345.	2047.	1291.	837.3	556.8	379.0
o-Xylene	4985.	3005.	1869.	1196.	785.3	528.2
p-Xylene	3787.	2309.	1452.	938.6	622.4	422.4
Cyclohexane	315.7	217.0	152.7	109.8	80.43	59.97
Methylcyclo-hexane	566.0	377.8	258.5	181.0	129.3	94.23
Tetrahydrofuran	451.0	300.4	205.2	143.4	102.4	74.47
Thiophene	570.7	381.7	261.7	183.6	131.5	95.92
Acetone	114.2	80.45	57.90	42.50	31.76	24.13
Methyl Ethyl Ketone	303.2	203.3	139.8	98.26	70.52	51.57
Methyl Propyl Ketone	742.3	475.0	312.5	210.8	145.5	102.6
Methyl Butyl Ketone	2078.	1263.	791.7	510.4	337.5	228.5
Acetylacetone	1961.	1222.	784.6	517.2	349.3	241.2
Methylene Chloride	130.7	92.50	66.90	49.33	37.03	28.25
Chloroform	364.1	243.9	167.4	117.6	84.26	61.55
1-Chloropentane	949.9	606.6	398.3	268.2	184.9	130.1
n-Butyronitrile	659.1	427.1	284.2	193.9	135.2	96.24
n-Valeronitrile	1857.	1142.	723.7	471.3	314.7	215.0
1,2-Dimethoxy-ethane	623.2	399.2	262.9	177.5	122.6	86.53

TABLE 39. Slopes m, Intercepts b, and Linear Regression Correlation Coefficients r for van't Hoff Plots of Ln V_g^o of Listed Probe-Solutes of Table 38 Against 10^3 T^{-1} with Fraction 2A of X-25LM R-45M

Probe Solute	m	- b	r
n-Pentane	2.812	5.452	0.9995_0
n-Hexane	3.384	6.252	0.9996_4
n-Heptane	3.927	6.986	0.9996_9
n-Octane	4.464	7.711	0.9997_6
3-Methylpentane	3.207	5.878	0.9996_3
2,3-Dimethylpentane	3.670	6.483	0.9995_5
3-Methylhexane	3.749	6.681	0.9996_8
3-Methylheptane	4.281	7.423	0.9997_3
1-Hexene	3.382	6.237	0.9995_1
1-Heptene	3.897	6.883	0.9997_6
1-Octene	4.441	7.673	0.9997_4
Benzene	3.726	6.166	0.9998_9
Toluene	4.287	6.909	0.9998_9
Ethylbenzene	4.663	7.267	0.9999_5
o-Xylene	4.806	7.341	0.9999_9
p-Xylene	4.697	7.253	0.9999_8
Cyclohexane	3.556	5.975	0.9997_3
Methylcyclohexane	3.839	6.325	0.9997_7
Tetrahydrofuran	3.856	6.610	0.9999_5
Thiophene	3.818	6.248	0.9998_3
Acetone	3.329	6.244	0.9997_9
Methyl Ethyl Ketone	3.793	6.798	0.9999_6
Methyl Propyl Ketone	4.238	7.369	0.9999_6
Methyl Butyl Ketone	4.727	7.953	0.9999_5
Acetylacetone	4.487	7.219	0.9999_7
Methylene Chloride	3.279	5.944	0.9996_0
Chloroform	3.806	6.658	0.9998_3
1-Chloropentane	4.257	7.185	0.9998_0
n-Butyronitrile	4.120	7.098	0.9999_1
n-Valeronitrile	4.617	7.702	0.9999_5
1,2-Dimethoxy-ethane	4.228	7.510	0.999_7

TABLE 40. Replicate Smoothed (van't Hoff) Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ for Listed Probe Solutes at Indicated Temperatures with Fraction 2B of X-25LM R-45M

	$V_g^o/cm^3\ g^{-1}$					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	45.45	33.84	25.67	19.79	15.49	12.30
n-Hexane	134.9	94.62	67.86	49.65	37.00	28.03
n-Heptane	390.2	258.3	175.4	121.9	86.54	62.64
n-Octane	1113.	695.5	447.5	295.7	200.1	138.5
3-Methylpentane	109.5	78.13	56.92	42.26	31.93	24.51
2,3-Dimethyl-pentane	274.4	187.1	130.7	93.25	67.86	50.28
3-Methylhexane	292.1	197.3	136.6	96.62	69.76	51.31
3-Methylheptane	807.3	515.2	338.1	227.6	156.7	110.3
1-Hexene	136.8	95.93	68.75	50.27	37.43	28.34
1-Heptene	391.5	259.9	176.9	123.3	87.70	63.62
1-Octene	1109.	695.4	448.9	297.5	201.9	140.1
Benzene	458.4	309.5	214.1	151.4	109.3	80.32
Toluene	1386.	881.7	576.9	387.2	266.0	186.7
Ethylbenzene	3408.	2074.	1301.	839.8	556.0	376.8
o-Xylene	5074.	3045.	1886.	1202.	786.6	527.3
p-Xylene	3867.	2346.	1468.	944.8	623.9	421.8
Cyclohexane	314.4	216.8	152.9	110.2	80.88	60.44
Methylcyclo-hexane	564.9	377.7	258.9	181.5	129.9	94.78
Tetrahydrofuran	435.9	290.4	198.4	138.7	99.03	72.05
Thiophene	573.2	383.0	262.4	183.9	131.5	95.90
Acetone	109.0	76.81	55.31	40.62	30.38	23.09
Methyl Ethyl Ketone	293.3	196.8	135.4	95.20	68.35	50.00
Methyl Propyl Ketone	719.5	460.6	303.1	204.6	141.3	99.60
Methyl Butyl Ketone	2032.	1233.	771.3	496.8	328.2	221.9
Acetylacetone	1969.	1217.	775.1	507.1	340.0	233.2
Methylene Chloride	131.8	93.10	67.17	49.42	37.02	28.19
Chloroform	364.8	244.4	167.8	117.9	84.52	61.75
1-Chloropentane	947.2	606.2	398.8	269.1	185.8	130.9
n-Butyronitrile	647.3	418.6	278.2	189.4	131.9	93.75
n-Valeronitrile	1841.	1127.	711.1	461.2	306.8	208.9
1,2-Dimethoxy-ethane	598.7	384.0	253.2	171.2	118.4	83.60

TABLE 41. Slopes m, Intercepts b, and Linear Regression Correlation Coefficients r for van't Hoff Plots of Ln V_g^o of Listed Probe-Solutes of Table 40 Against 10^3 T^{-1} with Fraction 2B of X-25LM R-45M

Probe Solute	m	- b	r
n-Pentane	2.799	5.415	0.9996_8
n-Hexane	3.363	6.191	0.9997_5
n-Heptane	3.917	6.954	0.9997_4
n-Octane	4.462	7.705	0.9998_0
3-Methylpentane	3.205	5.878	0.9998_4
2,3-Dimethylpentane	3.633	6.370	0.9998_4
3-Methylhexane	3.724	6.607	0.9993_0
3-Methylheptane	4.263	7.367	0.9998_2
1-Hexene	3.371	6.202	0.9997_9
1-Heptene	3.891	6.865	0.9997_5
1-Octene	4.429	7.601	0.9998_0
Benzene	3.729	6.173	0.9999_2
Toluene	4.292	6.924	0.9999_5
Ethylbenzene	4.715	7.420	0.9998_3
o-Xylene	4.848	7.460	0.9999_4
p-Xylene	4.744	7.390	0.9999_4
Cyclohexane	3.513	5.897	0.9998_2
Methylcyclohexane	3.822	6.271	0.9998_2
Tetrahydrofuran	3.854	6.636	0.9999_2
Thiophene	3.828	6.277	0.9999_6
Acetone	3.323	6.269	0.9998_4
Methyl Ethyl Ketone	3.788	6.814	0.9999_8
Methyl Propyl Ketone	4.234	7.387	0.9999_7
Methyl Butyl Ketone	4.742	8.025	0.9999_5
Acetylacetone	4.568	7.483	0.9999_9
Methylene Chloride	3.303	6.015	0.9999_5
Chloroform	3.863	6.647	0.9998_9
1-Chloropentane	4.237	7.122	0.9998_9
n-Butyronitrile	4.137	7.174	0.9999_7
n-Valeronitrile	4.660	7.854	0.9999_8
1,2-Dimethoxy-ethane	4.215	7.509	0.9999_6

TABLE 42. Smoothed (van't Hoff) Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ for Listed Probe Solutes at Indicated Temperatures with Fraction 3A of X-25LM R-45M

	$V_g^o/cm^3\ g^{-1}$					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	47.09	34.94	26.41	20.31	15.85	12.55
n-Hexane	139.3	97.50	69.75	50.92	37.85	28.62
n-Heptane	405.0	267.3	181.0	125.5	88.86	64.17
n-Octane	1157.	721.2	462.9	305.1	206.0	142.3
3-Methylpentane	114.1	80.97	58.69	43.37	32.62	24.93
2,3-Dimethyl-pentane	285.4	193.8	134.8	95.83	69.49	51.32
3-Methylhexane	304.6	205.0	141.4	99.68	71.73	52.59
3-Methylheptane	844.4	536.8	350.9	235.3	161.5	113.3
1-Hexene	140.5	98.27	70.28	51.28	38.11	28.81
1-Heptene	404.0	267.2	181.4	126.0	89.38	64.67
1-Octene	1148.	717.1	461.3	304.7	206.2	142.7
Benzene	456.4	308.1	213.1	150.7	108.7	79.89
Toluene	1389.	883.2	577.5	387.3	265.9	186.5
Ethylbenzene	3312.	2034.	1287.	837.1	558.3	381.0
o-Xylene	5037.	3026.	1877.	1197.	784.3	526.2
p-Xylene	3814.	2322.	1458.	941.0	623.2	422.4
Cyclohexane	323.7	222.5	156.5	112.5	82.37	61.41
Methylcyclo-hexane	583.3	388.9	265.9	186.0	132.9	96.71
Tetrahydrofuran	423.3	282.4	193.2	135.2	96.59	70.35
Thiophene	564.4	377.5	258.8	181.5	129.9	94.82
Acetone	101.5	72.03	52.20	38.56	29.00	22.16
Methyl Ethyl Ketone	274.4	184.9	127.7	90.16	64.97	47.69
Methyl Propyl Ketone	681.3	437.1	288.3	194.9	134.8	95.23
Methyl Butyl Ketone	1912.	1164.	730.2	471.2	312.0	211.4
Acetylacetone	1657.	1149.	732.7	479.9	322.2	221.2
Methylene Chloride	127.9	90.11	64.89	47.66	35.64	27.10
Chloroform	351.4	235.6	161.9	113.7	81.59	59.64
1-Chloropentane	949.7	606.5	398.3	268.2	184.9	130.1
n-Butyronitrile	597.4	386.6	257.0	175.1	122.0	86.73
n-Valeronitrile	1712.	1046.	659.5	427.3	284.0	193.1
1,2-Dimethoxy-ethane	572.8	368.7	243.9	165.4	114.8	81.27

TABLE 43. Slopes m, Intercepts b, and Linear Regression Correlation Coefficients r for van't Hoff Plots of Ln V_g^o of Listed Probe-Solutes of Table 42 Against 10^3 T^{-1} with Fraction 3A of X-25LM R-45M

Probe Solute	m	- b	r
n-Pentane	2.832	5.489	0.9995_5
n-Hexane	3.389	6.242	0.9995_3
n-Heptane	3.944	7.008	0.9996_1
n-Octane	4.488	7.750	0.9996_3
3-Methylpentane	3.257	6.005	0.9996_8
2,3-Dimethylpentane	3.674	6.464	0.9996_0
3-Methylhexane	3.761	6.687	0.9995_9
3-Methylheptane	4.301	7.449	0.9996_1
1-Hexene	3.393	6.247	0.9996_5
1-Heptene	3.923	6.939	0.9995_9
1-Octene	4.464	7.680	0.9996_6
Benzene	3.731	6.186	0.9998_3
Toluene	4.300	6.947	0.9998_2
Ethylbenzene	4.630	7.168	0.9998_7
o-Xylene	4.837	7.430	0.9999_2
p-Xylene	4.711	7.295	0.9999_2
Cyclohexane	3.559	5.961	0.9996_1
Methylcyclohexane	3.847	6.323	0.9996_5
Tetrahydrofuran	3.843	6.628	0.9999_5
Thiophene	3.820	6.264	0.9998_7
Acetone	3.259	6.130	0.9998_0
Methyl Ethyl Ketone	3.746	6.743	0.9998_9
Methyl Propyl Ketone	4.213	7.374	0.9998_7
Methyl Butyl Ketone	4.715	7.996	0.9999_2
Acetylacetone	4.556	7.501	0.9998_7
Methylene Chloride	3.322	6.108	0.9999_7
Chloroform	3.798	6.666	0.9999_1
1-Chloropentane	4.256	7.183	0.9998_5
n-Butyronitrile	4.132	7.238	0.9998_8
n-Valeronitrile	4.672	7.965	0.9999_4
1,2-Dimethoxy-ethane	4.181	7.442	0.9998_6

TABLE 44. Smoothed (van't Hoff) Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ for Listed Probe Solutes at Indicated Temperatures with Fraction 3B of X-25LM R-45M

	$V_g^o/cm^3\ g^{-1}$					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	50.96	37.42	28.01	21.34	16.51	12.96
n-Hexane	151.3	104.7	74.21	53.68	39.56	29.67
n-Heptane	438.3	286.5	192.2	132.1	92.81	66.51
n-Octane	1255.	773.6	491.5	320.8	214.7	147.0
3-Methylpentane	122.8	86.55	62.35	45.81	34.27	26.06
2,3-Dimethyl-pentane	303.2	205.0	142.0	100.6	72.65	53.46
3-Methylhexane	330.1	219.7	150.0	104.7	74.68	54.28
3-Methylheptane	917.8	576.4	372.6	247.2	168.0	116.7
1-Hexene	150.1	104.3	74.10	53.75	39.72	29.86
1-Heptene	434.1	284.5	191.4	131.8	92.81	66.66
1-Octene	1232.	762.8	486.5	318.8	214.1	147.1
Benzene	470.7	316.9	218.6	154.2	111.0	81.43
Toluene	1439.	911.0	593.0	396.2	270.9	189.3
Ethylbenzene	3486.	2121.	1331.	858.9	568.5	385.2
o-Xylene	4102.	2460.	1523.	970.2	634.6	425.1
p-Xylene	5329.	3169.	1946.	1231.	799.2	531.9
Cyclohexane	348.5	237.3	165.5	117.9	85.73	63.45
Methylcyclo-hexane	633.5	417.1	281.9	195.0	137.8	99.36
Tetrahydrofuran	417.0	278.3	190.5	133.4	95.33	69.46
Thiophene	574.6	383.7	262.8	184.1	131.6	95.96
Acetone	101.8	72.13	52.20	38.52	28.94	22.09
Methyl Ethyl Ketone	273.4	183.8	126.6	89.20	64.14	46.99
Methyl Propyl Ketone	675.3	432.9	285.2	192.7	133.2	93.99
Methyl Butyl Ketone	1905.	1156.	723.9	466.1	308.1	208.3
Acetylacetone	1917.	1190.	760.7	499.6	336.3	231.5
Methylene Chloride	125.9	89.51	65.00	48.12	36.25	27.75
Chloroform	347.4	234.0	161.5	114.0	82.12	60.26
1-Chloropentane	986.0	627.0	410.0	275.1	188.9	132.5
n-Butyronitrile	557.6	365.0	245.3	168.8	118.8	85.22
n-Valeronitrile	1593.	986.6	629.3	412.4	277.0	190.3

TABLE 45. Slopes m, Intercepts b, and Linear Regression Correlation Coefficients r for van't Hoff Plots of Ln V_g^o of Listed Probe-Solutes of Table 44 Against 10^3 T^{-1} with Fraction 3B of X-25LM R-45M

Probe Solute	m	- b	r
n-Pentane	2.931	5.737	0.9997_8
n-Hexane	3.488	6.485	0.9998_5
n-Heptane	4.037	7.234	0.9998_9
n-Octane	4.591	8.010	0.9999_0
3-Methylpentane	3.319	6.137	0.9998_6
2,3-Dimethylpentane	3.716	6.544	0.9999_9
3-Methylhexane	3.865	6.951	0.9999_3
3-Methylheptane	4.416	7.745	0.9999_3
1-Hexene	3.457	6.393	0.9998_7
1-Heptene	4.012	7.160	0.9998_8
1-Octene	4.551	7.896	0.9999_1
Benzene	3.756	6.237	0.9999_6
Toluene	4.343	7.056	0.9999_6
Ethylbenzene	4.716	7.401	0.9999_9
o-Xylene	4.853	7.691	0.9999_9
p-Xylene	4.934	7.696	0.9999_8
Cyclohexane	3.648	6.179	0.9999_2
Methylcyclohexane	3.966	6.633	0.9998_5
Tetrahydrofuran	3.838	6.626	0.9999_6
Thiophene	3.832	6.287	0.9999_7
Acetone	3.271	6.168	0.9999_4
Methyl Ethyl Ketone	3.771	6.828	0.9999_7
Methyl Propyl Ketone	4.222	7.413	0.9999_9
Methyl Butyl Ketone	4.739	8.079	0.9999_9
Acetylacetone	4.526	7.373	0.9998_6
Methylene Chloride	3.238	5.845	0.9999_8
Chloroform	3.751	6.523	0.9999_7
1-Chloropentane	4.298	7.284	0.9999_7
n-Butyronitrile	4.022	6.943	0.9999_8
n-Valeronitrile	4.550	7.637	0.9999_9

TABLE 46. Replicate Smoothed (van't Hoff) Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ for Listed Probe Solutes at Indicated Temperatures with Fraction 4A of X-25LM R-45M

	$V_g^o/cm^3\ g^{-1}$					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	49.22	36.42	27.46	21.06	16.40	12.96
n-Hexane	146.2	101.8	72.55	52.75	39.07	29.44
n-Heptane	422.0	277.5	187.2	129.3	91.31	65.74
n-Octane	1204.	748.2	478.9	314.9	212.2	146.2
3-Methylpentane	118.9	84.17	60.86	44.87	33.67	25.68
2,3-Dimethyl-pentane	298.6	202.0	140.0	99.18	71.69	52.79
3-Methylhexane	318.3	213.2	146.4	102.9	73.76	53.90
3-Methylheptane	880.7	557.5	363.1	242.6	166.0	116.0
1-Hexene	145.7	101.6	72.49	52.77	39.13	29.51
1-Heptene	419.6	276.8	187.3	129.8	91.84	66.29
1-Octene	1194.	743.1	476.3	313.6	211.5	145.9
Benzene	466.7	314.3	216.9	153.1	110.3	80.90
Toluene	1420.	900.3	587.4	393.1	269.4	188.6
Ethylbenzene	3446.	2101.	1320.	853.3	565.7	383.8
o-Xylene	5259.	3136.	1931.	1224.	796.9	531.5
p-Xylene	3997.	2413.	1503.	962.7	633.1	426.3
Cyclohexane	338.6	231.9	162.6	116.4	85.04	63.22
Methylcyclo-hexane	609.0	404.6	275.8	192.3	137.0	99.44
Tetrahydrofuran	414.9	275.4	187.5	130.6	92.95	67.43
Thiophene	577.9	385.3	263.5	184.3	131.6	95.83
Acetone	97.35	69.13	50.14	37.08	27.90	21.34
Methyl Ethyl Ketone	264.3	178.0	122.9	86.73	62.47	45.84
Methyl Propyl Ketone	658.4	421.5	277.4	187.2	129.2	91.12
Methyl Butyl Ketone	1856.	1126.	704.5	453.4	299.4	202.4
Acetylacetone	1806.	1119.	714.2	468.3	314.7	216.3
Methylene Chloride	128.1	90.52	65.34	48.10	36.05	27.46
Chloroform	353.3	236.8	162.7	114.3	81.98	59.92
1-Chloropentane	976.8	621.4	406.5	272.8	187.4	131.5
n-Butyronitrile	601.8	383.8	251.7	169.3	116.5	81.90
n-Valeronitrile	1629.	998.4	630.7	409.6	272.8	185.9
1,2-Dimethoxy-ethane	547.2	350.7	231.0	156.0	107.8	76.11

TABLE 47. Slopes m, Intercepts b, and Linear Regression Correlation Coefficients r for van't Hoff Plots of Ln V_g^o of Listed Probe-Solutes of Table 46 Against 10^3 T^{-1} with Fraction 4A of X-25LM R-45M

Probe Solute	m	-b	r
n-Pentane	2.857	5.530	0.9996_8
n-Hexane	3.431	6.333	0.9997_8
n-Heptane	3.981	7.087	0.9997_1
n-Octane	4.514	7.799	0.9998_4
3-Methylpentane	3.282	6.047	0.9997_9
2,3-Dimethylpentane	3.710	6.540	0.9997_9
3-Methylhexane	3.802	6.779	0.9998_4
3-Methylheptane	4.340	7.537	0.9998_4
1-Hexene	3.419	6.296	0.9998_1
1-Heptene	3.951	6.994	0.9998_4
1-Octene	4.500	7.760	0.9998_2
Benzene	3.752	6.232	0.9998_8
Toluene	4.322	7.000	0.9999_1
Ethylbenzene	4.700	7.357	0.9999_4
o-Xylene	4.907	7.620	0.9999_9
p-Xylene	4.792	7.515	0.9999_8
Cyclohexane	3.593	6.028	0.9998_2
Methylcyclohexane	3.880	6.388	0.9998_2
Tetrahydrofuran	3.890	6.805	0.9999_9
Thiophene	3.847	6.331	0.9999_2
Acetone	3.250	6.142	0.9999_1
Methyl Ethyl Ketone	3.752	6.798	0.9999_6
Methyl Propyl Ketone	4.234	7.478	0.9999_8
Methyl Butyl Ketone	4.745	8.125	0.9999_9
Acetylacetone	4.543	7.488	0.9999_0
Methylene Chloride	3.298	6.025	0.9999_6
Chloroform	3.799	6.665	0.9999_2
1-Chloropentane	4.294	7.280	0.9999_2
n-Butyronitrile	4.270	7.686	0.9990_8
n-Valeronitrile	4.648	7.936	0.9999_9
1,2-Dimethoxy-ethane	4.224	7.628	0.9998_5

TABLE 48. Smoothed (van't Hoff) Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ for Listed Probe Solutes at Indicated Temperatures with Fraction 4A of X-25LM R-45M

	$V_g^o/cm^3\ g^{-1}$					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	46.65	34.68	26.26	20.22	15.81	12.53
n-Hexane	138.7	97.04	69.42	50.67	37.67	28.48
n-Heptane	400.2	264.4	179.3	124.4	88.21	63.76
n-Octane	1142.	712.7	458.0	302.2	204.3	141.2
3-Methylpentane	114.1	80.75	58.38	43.04	32.29	24.63
2,3-Dimethyl-pentane	283.9	192.6	133.8	95.06	68.87	50.82
3-Methylhexane	303.1	203.7	140.3	98.79	71.02	52.01
3-Methylheptane	838.4	532.6	348.0	233.2	160.0	112.1
1-Hexene	138.3	97.03	69.57	50.89	37.92	28.71
1-Heptene	398.5	263.9	179.3	124.7	88.56	64.12
1-Octene	1128.	706.2	455.0	301.0	204.0	141.3
Benzene	454.4	306.1	211.3	149.2	107.4	78.84
Toluene	1379.	875.5	571.7	383.0	262.6	184.0
Ethylbenzene	3363.	2047.	1285.	829.4	549.2	372.2
o-Xylene	5069.	3029.	1869.	1187.	774.1	517.2
p-Xylene	3866.	2335.	1455.	932.4	613.3	413.1
Cyclohexane	324.6	222.6	156.3	112.1	81.97	61.01
Methylcyclo-hexane	581.2	387.2	264.6	184.9	132.0	96.04
Tetrahydrofuran	401.7	266.9	181.9	126.9	90.36	65.60
Thiophene	563.6	375.6	256.7	179.5	128.2	93.26
Acetone	99.50	69.88	50.17	36.74	27.40	20.77
Methyl Ethyl Ketone	264.6	177.2	121.6	85.36	61.17	44.67
Methyl Propyl Ketone	654.8	417.1	273.2	183.6	126.2	88.67
Methyl Butyl Ketone	1848.	1115.	693.7	444.2	291.9	196.5
Acetylacetone	1792.	1102.	699.1	455.6	304.4	208.1
Methylene Chloride	126.6	89.27	64.33	47.28	35.38	26.91
Chloroform	349.4	233.4	159.9	112.0	80.15	58.44
1-Chloropentane	944.6	601.2	393.4	264.1	181.5	127.4
n-Butyronitrile	573.9	369.8	244.9	166.2	115.4	81.79
n-Valeronitrile	1645.	1001.	628.5	405.7	268.6	182.1
1,2-Dimethoxy-ethane	534.5	342.4	225.5	152.2	105.2	74.19

TABLE 49. Slopes m, Intercepts b, and Linear Regression Correlation Coefficients r for van't Hoff Plots of Ln V_g^o of Listed Probe-Solutes of Table 48 Against 10^3 T^{-1} with Fraction 4B of X-25LM R-45M

Probe Solute	m	- b	r
n-Pentane	2.814	5.440	0.9998_6
n-Hexane	3.390	6.249	0.9998_2
n-Heptane	3.933	6.981	0.9998_7
n-Octane	4.475	7.723	0.9998_9
3-Methylpentane	3.283	6.093	0.9998_8
2,3-Dimethylpentane	3.683	6.502	0.9998_4
3-Methylhexane	3.774	6.734	0.9998_2
3-Methylheptane	4.307	7.477	0.9998_8
1-Hexene	3.367	6.175	0.9999_1
1-Heptene	3.912	6.916	0.9999_0
1-Octene	4.448	7.644	0.9999_0
Benzene	3.750	6.252	0.9999_6
Toluene	4.313	6.998	0.9999_6
Ethylbenzene	4.713	7.427	0.9999_7
o-Xylene	4.887	7.590	0.9999_8
p-Xylene	4.788	7.535	0.9999_2
Cyclohexane	3.579	6.023	0.9999_0
Methylcyclohexane	3.855	6.351	0.9998_9
Tetrahydrofuran	3.880	6.804	0.9999_7
Thiophene	3.852	6.372	0.9999_6
Acetone	3.354	6.464	0.9997_9
Methyl Ethyl Ketone	3.809	6.986	0.9999_9
Methyl Propyl Ketone	4.281	7.637	0.9999_9
Methyl Butyl Ketone	4.799	8.309	0.9999_9
Acetylacetone	4.610	7.716	0.9999_8
Methylene Chloride	3.315	6.096	0.9999_6
Chloroform	3.829	6.774	0.9999_6
1-Chloropentane	4.290	7.301	0.9999_3
n-Butyronitrile	4.172	7.408	0.9999_9
n-Valeronitrile	4.712	8.140	0.9999_8
1,2-Dimethoxy-ethane	4.228	766.7	0.9999_7

TABLE 50. Replicate Smoothed (van't Hoff) Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ for Listed Probe Solutes at Indicated Temperatures with Fraction 5A of X-25LM R-45M

	$V_g^o/cm^3\ g^{-1}$					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	49.95	36.72	27.51	20.98	16.25	12.77
n-Hexane	148.3	102.6	72.70	52.57	38.74	29.05
n-Heptane	429.6	280.5	188.0	129.1	90.61	64.88
n-Octane	1233.	759.3	481.9	314.3	210.2	143.8
3-Methylpentane	120.2	84.62	60.88	44.67	33.38	25.35
2,3-Dimethyl-pentane	301.9	203.0	139.9	98.59	70.90	51.96
3-Methylhexane	322.4	214.7	146.7	102.5	73.13	53.19
3-Methylheptane	893.6	562.1	363.9	241.8	164.5	114.4
1-Hexene	146.2	101.6	72.18	52.34	38.68	29.07
1-Heptene	421.7	276.5	186.1	128.2	90.33	64.90
1-Octene	1202.	744.1	474.4	310.8	208.7	143.3
Benzene	452.4	304.5	210.0	148.1	106.6	78.16
Toluene	1380.	874.8	570.5	381.8	261.5	183.0
Ethylbenzene	3388.	2056.	1287.	829.0	547.7	370.4
o-Xylene	5120.	3047.	1872.	1185.	770.0	512.7
p-Xylene	3922.	2358.	1463.	934.6	612.7	411.3
Cyclohexane	342.6	232.9	162.1	115.4	83.73	61.88
Methylcyclo-hexane	617.0	407.0	275.5	190.9	135.1	97.52
Tetrahydrofuran	379.0	253.0	173.2	121.3	86.70	63.18
Thiophene	552.9	368.8	252.3	176.6	126.2	91.89
Acetone	89.93	63.58	45.92	33.82	25.36	19.33
Methyl Ethyl Ketone	241.2	162.8	112.6	79.58	57.41	42.19
Methyl Propyl Ketone	607.4	388.4	255.3	172.1	118.7	83.66
Methyl Butyl Ketone	1696.	1030.	645.3	415.8	274.8	185.9
Acetylacetone	1690.	1046.	666.4	436.4	292.9	201.1
Methylene Chloride	119.4	84.72	61.42	45.39	34.14	26.10
Chloroform	329.0	221.3	152.6	107.6	77.39	56.73
1-Chloropentane	947.7	602.1	393.5	263.8	181.0	126.9
n-Butyronitrile	500.3	327.2	219.7	151.1	106.2	76.17
n-Valeronitrile	1422.	879.5	560.6	367.1	246.4	169.2
1,2-Dimethoxy-ethane	497.9	320.4	211.8	143.6	99.54	70.46

TABLE 51. Slopes m, Intercepts b, and Linear Regression Correlation Coefficients r for van't Hoff Plots of $\ln V_g^o$ of Listed Probe-Solutes of Table 50 Against $10^3\ T^{-1}$ with Fraction 5A of X-25LM R-45M

Probe Solute	m	- b	r
n-Pentane	2.921	5.723	0.9998_4
n-Hexane	3.490	6.514	0.9998_9
n-Heptane	4.047	7.288	0.9998_9
n-Octane	4.600	8.059	0.9999_0
3-Methylpentane	3.332	6.203	0.9998_5
2,3-Dimethylpentane	3.768	6.719	0.9998_6
3-Methylhexane	3.858	6.950	0.9998_9
3-Methylheptane	4.401	7.722	0.9998_8
1-Hexene	3.459	6.424	0.9998_6
1-Heptene	4.007	7.174	0.9999_0
1-Octene	4.554	7.931	0.9999_0
Benzene	3.760	6.287	0.9999_1
Toluene	4.325	7.037	0.9998_4
Ethylbenzene	4.739	7.504	0.9999_7
o-Xylene	4.927	7.712	0.9999_3
p-Xylene	4.828	7.652	0.9999_1
Cyclohexane	3.664	6.250	0.9998_7
Methylcyclohexane	3.950	6.605	0.9999_1
Tetrahydrofuran	3.836	6.715	0.9998_9
Thiophene	3.842	6.360	0.9999_2
Acetone	3.392	6.361	0.9999_0
Methyl Ethyl Ketone	3.733	6.829	0.9999_9
Methyl Propyl Ketone	4.245	7.593	0.9999_4
Methyl Butyl Ketone	4.733	8.178	0.9999_7
Acetylacetone	4.558	7.604	0.9999_4
Methylene Chloride	3.256	5.951	0.9998_9
Chloroform	3.764	6.820	0.9999_3
1-Chloropentane	4.305	7.348	0.9999_2
n-Butyronitrile	4.030	7.079	0.9999_3
n-Valeronitrile	4.557	7.774	0.9999_4
1,2-Dimethoxy-ethane	4.187	7.600	0.999_2

TABLE 52. Molar Specific Retention Volumes V_g^o'/cm^3 mol^{-1} for Listed Probe-Solutes with Indicated Lots of R-45M at 30° and 50°C

A. Compounds whose retentions at 30°C fail to distinguish between 14LM and 20LM

	10^{-3} V_g^o'/cm^3 mol^{-1}				
Solute	10LM	14LM	20LM	25LM	120HM
n-Hexane	141.9	184.3	197.0	212.1	468.9
3-Methylhexane	310.3	399.0	429.4	495.4	975.2
1-Hexene	141.9	186.1	196.7	227.7	472.6
Cyclohexane	327.8	424.6	454.8	525.0	1088.
Benzene	492.0	628.4	643.0	752.4	1498.
Tetrahydrofuran	490.0	617.0	630.1	706.8	1280.
1-Chloropentane	1020.	1318.	1340.	1549.	3106.

B. Compounds whose retentions at 30° and 50°C appear to reflect the molecular weight difference between 14LM and 20LM

Thiophene					
30°C	610.1	788.5	785.6	935.6	1874.
Acetone					
30°C	120.5	151.1	150.4	175.6	334.8
Chloroform					
30°C	397.6	504.4	498.0	588.4	1178.
50°C	182.5	233.3	231.3	272.5	534.3
n-Valeronitrile					
30°C	2095.	2623.	2502.	2924.	5683.
50°C	811.2	1031.	990.6	1152.	2142.

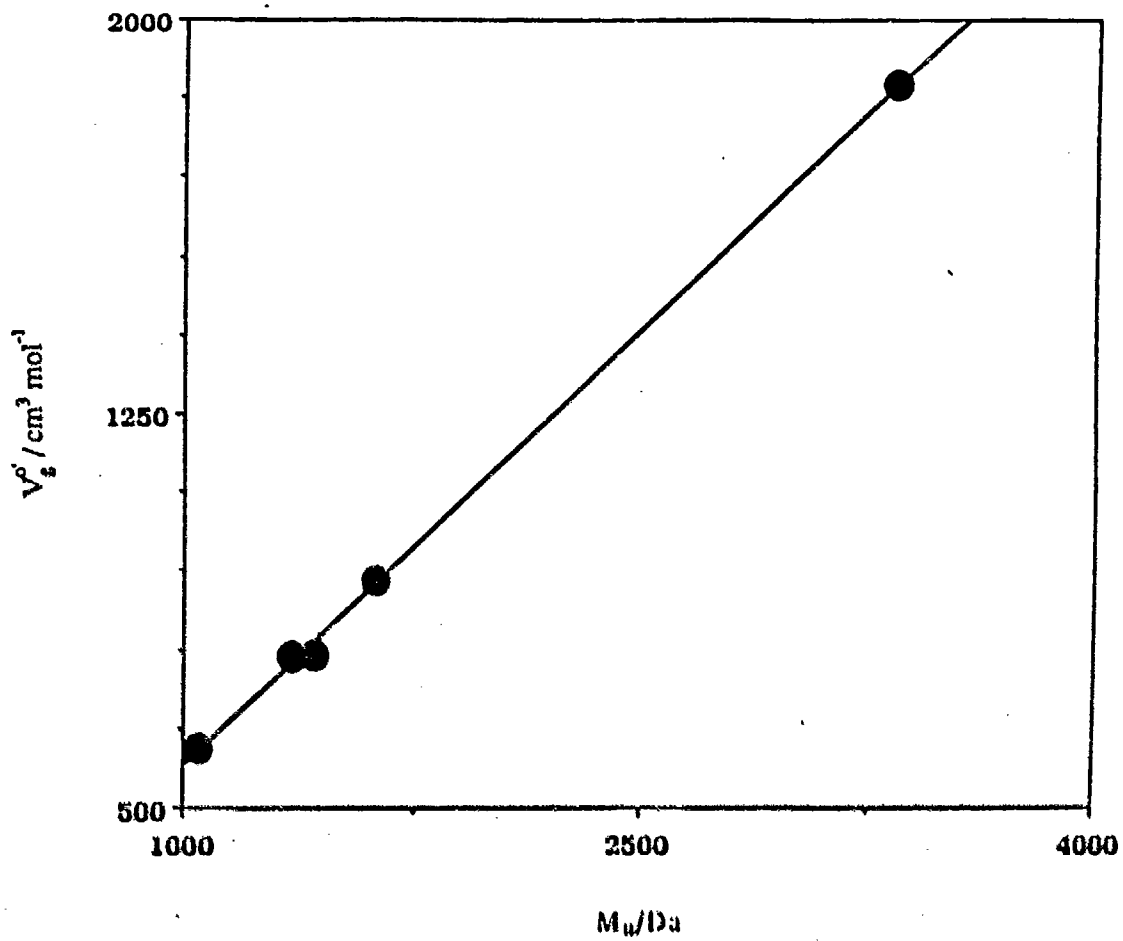

FIGURE 8. Test of regression of molar specific retention volume V_g^0 /cm^3 mol^{-1} against stationary-phase number-average molecular weight M_n/Da for thiophene solute at 30°C.

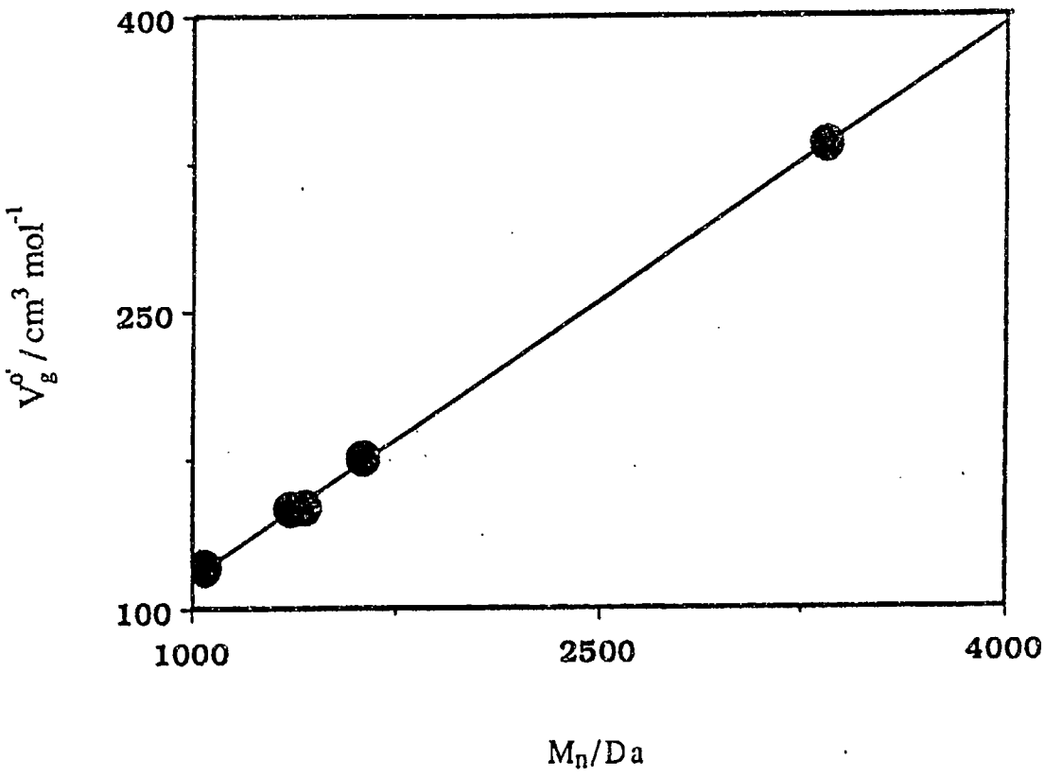

FIGURE 6. As in Figure 5; acetone solute.

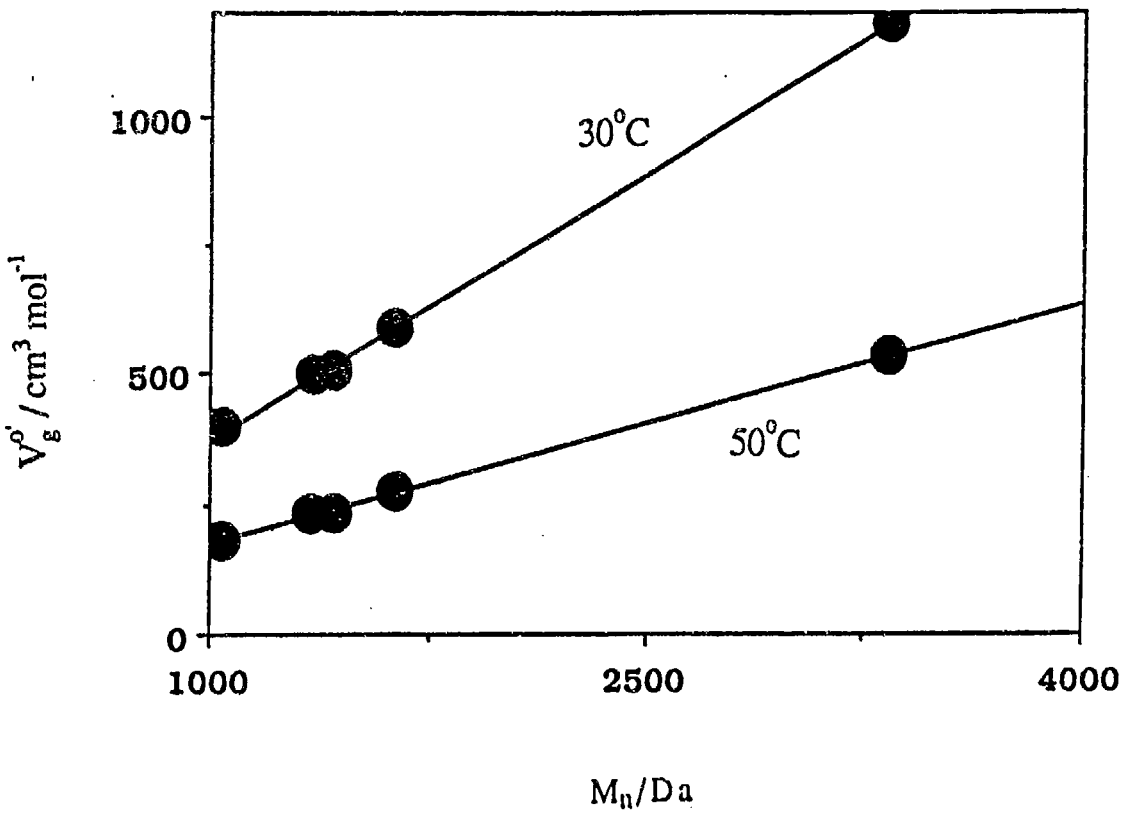

FIGURE 7. As in Figure 5; chloroform solute.

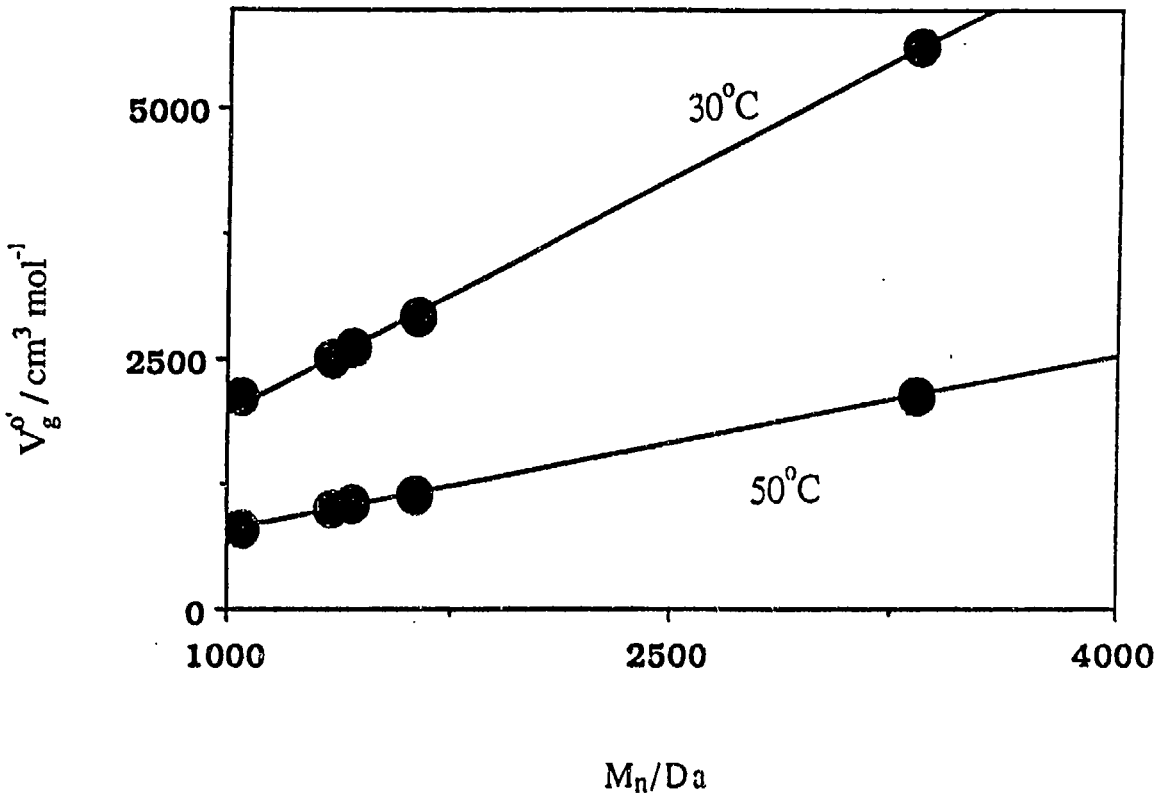

FIGURE 8. As in Figure 5; valeronitrile solute.

Regressions of Conventional-Form Specific Retention Volumes. The conventional-form specific retention volumes $V_g^o/cm^3\ g^{-1}$ of the four promising solutes of Table 52.B were next examined in terms of the molecular weights of the ARCO lots of R-45M. The relevant data are provided in Table 53. The retentions only of chloroform at 30°C and valeronitrile at 30° and 50°C provide significant distinction between the R-45M. (In contrast, those of thiophene for example with 10LM and 20LM are nearly identical and so, this solute is not suitable as a molecular-weight probe.)

TABLE 53. Conventional-Form Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ of Listed Probe-Solutes with Indicated Lots of R-45M at 30° and 50°C

A. Compounds whose retentions fail to reflect significant differences in the M_n of 10LM, 14LM, and 20LM

	$V_g^o/cm^3\ g^{-1}$				
Solute	10LM	14LM	20LM	25LM	120HM
Thiophene 30°C	586.6	555.3	581.9	574.0	561.8
Acetone 30°C	115.9	106.4	111.4	107.7	100.4
Chloroform 50°C	175.5	164.3	171.3	167.2	160.2

B. Compounds whose retentions appear to reflect molecular weight differences between 10LM, 14LM, and 20LM

Chloroform 30°C	382.3	355.2	368.9	361.0	353.3
Valeronitrile 30°C	2014.	1847.	1853.	1794.	1704.
50°C	780.0	726.2	733.8	706.6	642.4

As shown below in Figure 9, plots of the V_g^o e.g. of valeronitrile against stationary-phase molecular weight were curved. Nevertheless, a plot of the specific retention volumes of this solute against inverse molecular weight at 50°C, Figure 10, gave a near-perfect correlation coefficient of 0.99996. (The analogous plots for chloroform were, however, not linear.) Table 54 confirms the goodness of fit of the linear regression. Thus, the number-average molecular weight of R-45M can be assessed simply by measuring the specific retention volumes of valeronitrile at 50°C.

Encouraged by the success shown in Figure 10 and Table 54, the regressions of all solutes at all temperatures as a function of inverse molecular weight were examined at this point. Several additional solutes at various temperatures were thereby identified also as good indicators of the stationary-phase molecular weight. The relevant plots of specific retention volume against inverse M are provided in Figures 11-14.

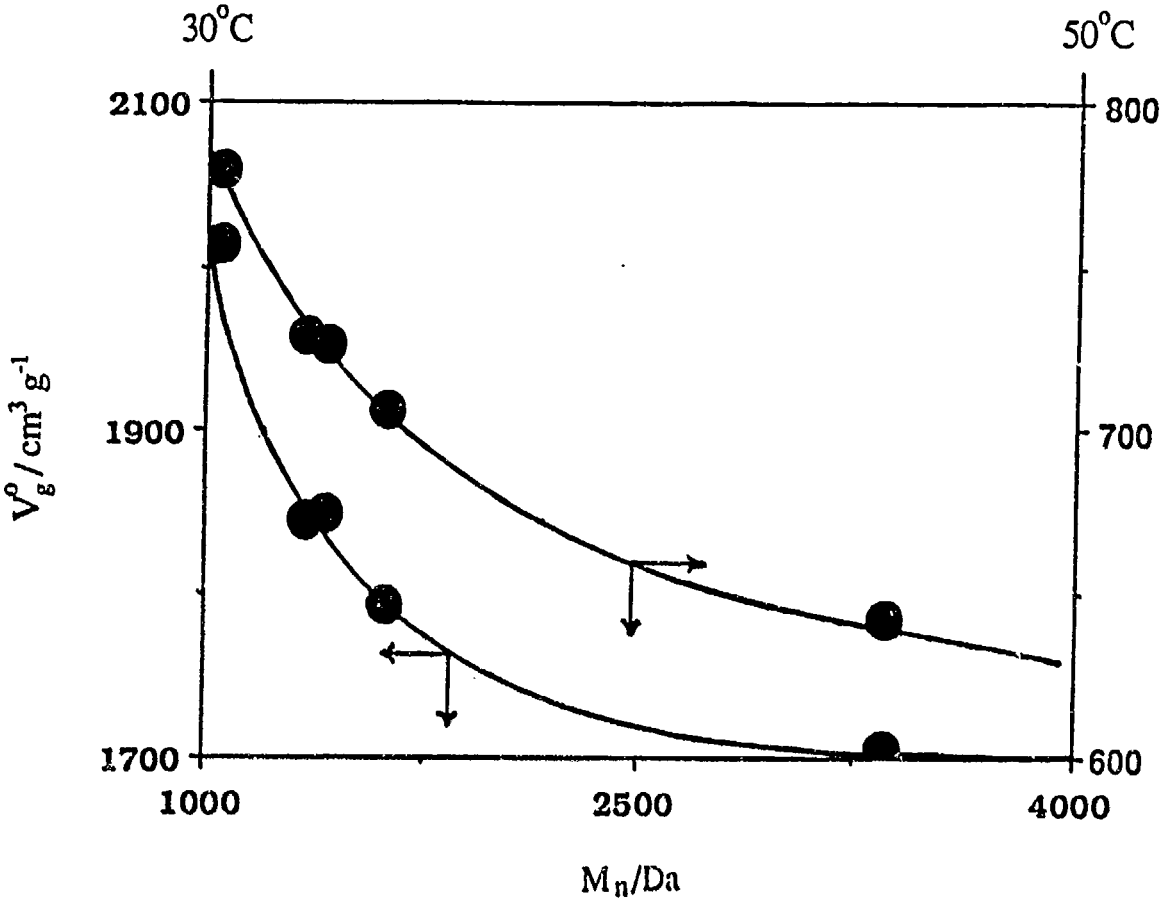

FIGURE 9. Plots of conventional-form specific retention volumes V_g^o/cm^3 g^{-1} of valeronitrile at 30° and 50°C against stationary-phase molecular weight.

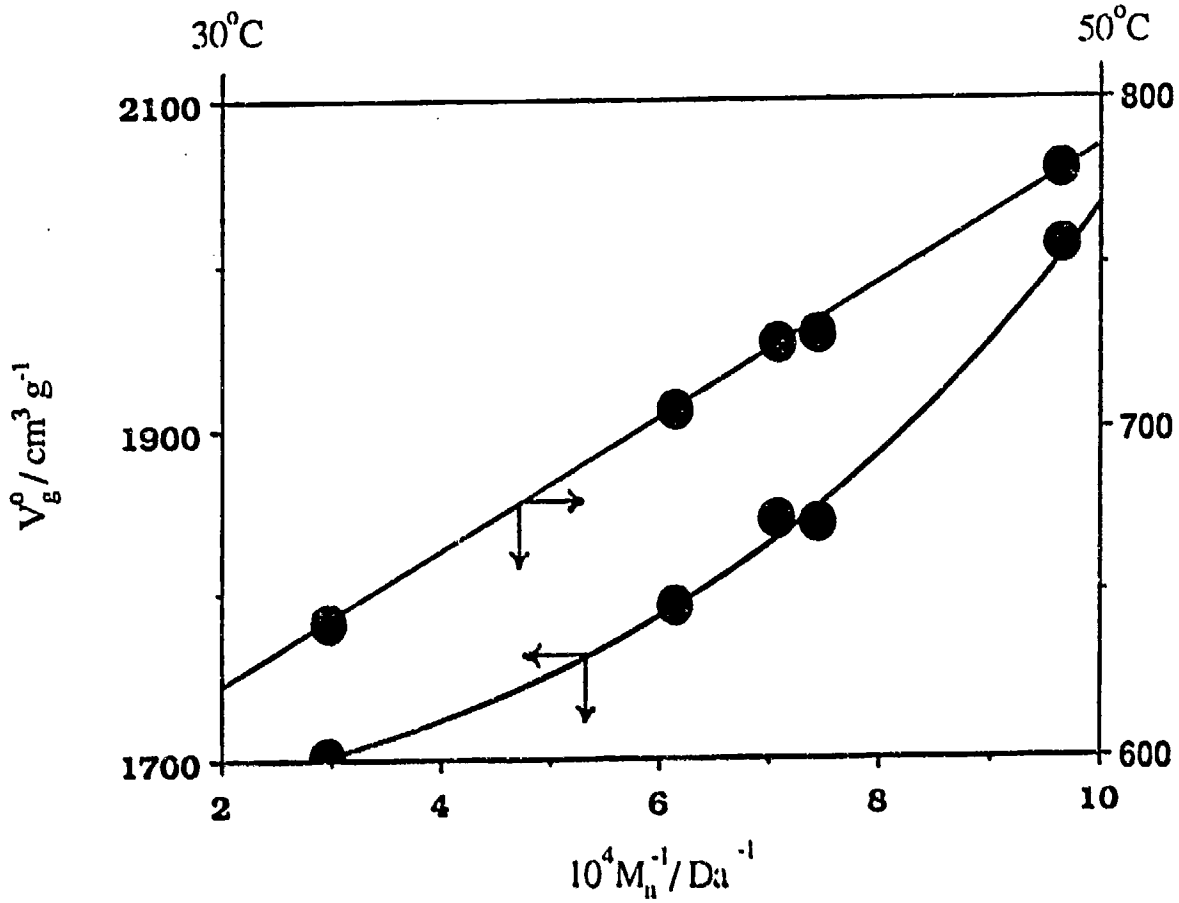

FIGURE 10. As in Figure 9; abscissa of inverse molecular weight.

TABLE 54. Test of Goodness of Fit of Linear Regression Shown in Figure 10

Lot of R-45M	Smoothed M_n/Da	Mfr. Claimed M_n/Da
10LM	1038	1040
14LM	1419	1420
20LM	1349	1350
25LM	1638	1630
120HM	3315	3335

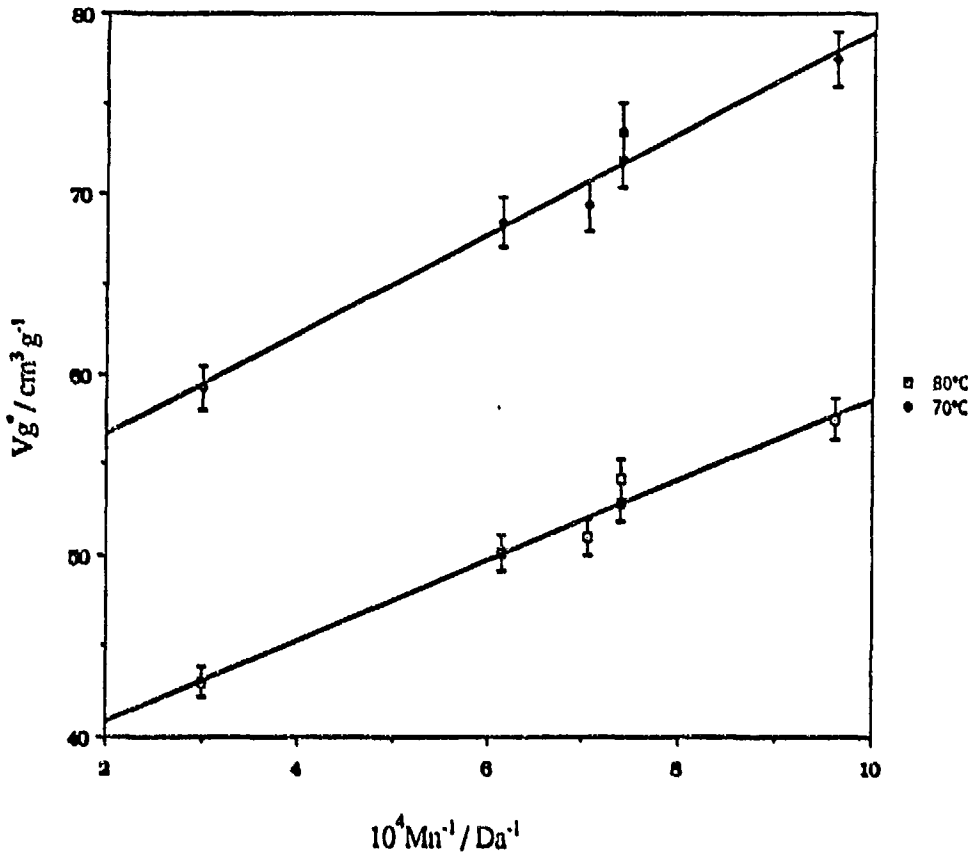

FIGURE 11 Plots of specific retention volumes of methyl ethyl ketone against inverse molecular weight of R-45M stationary phases at 70 and 80°C.

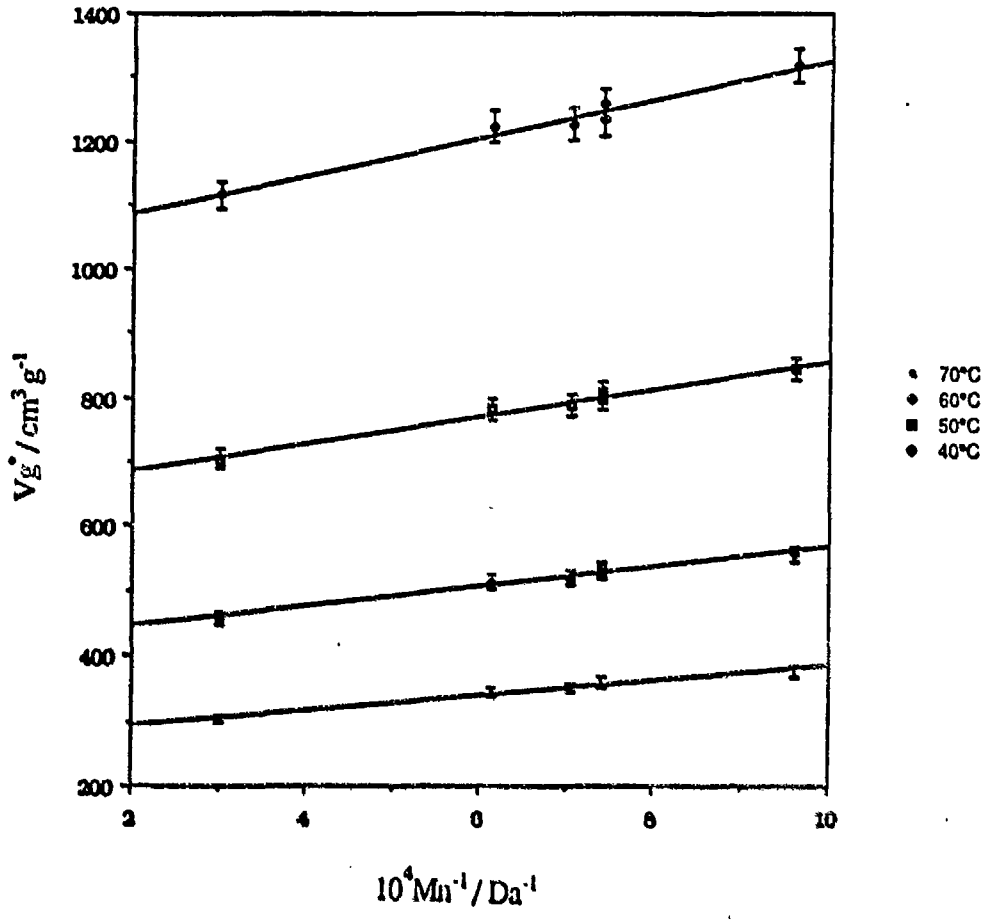

FIGURE 12. As in Figure 11; acetylacetone solute at 40-70 °C.

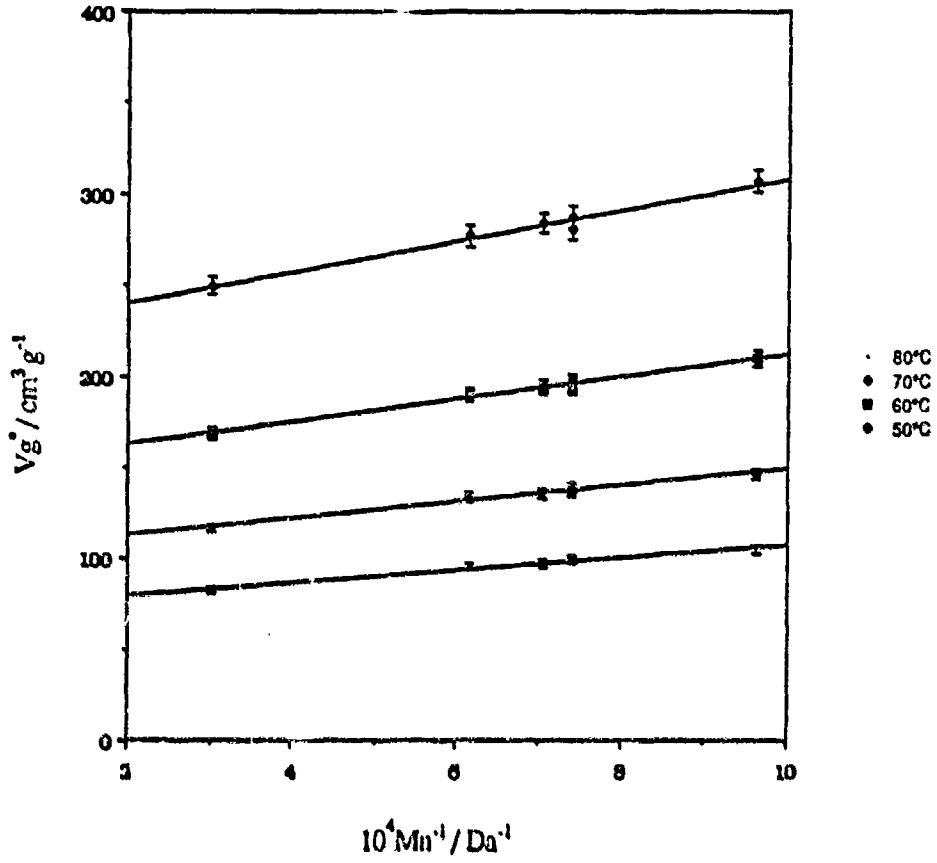

FIGURE 13. As in Figure 11; butyronitrile solute at 50-80°C.

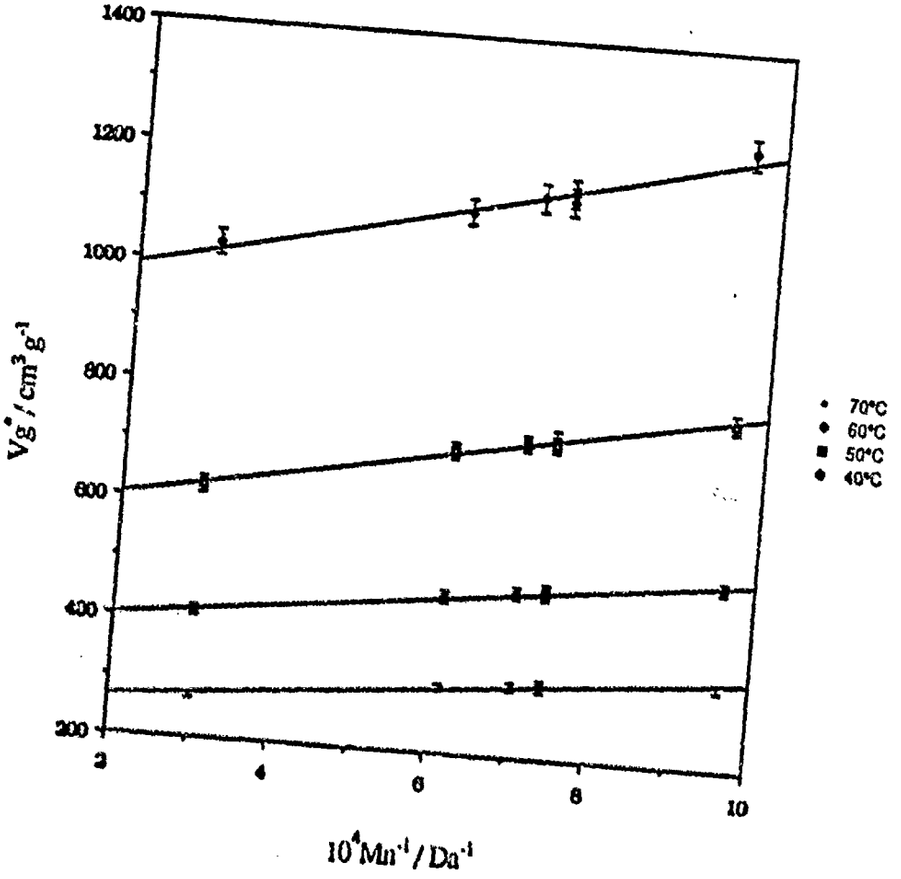

FIGURE 14. As in Figure 11; valeronitrile solute at 40–70°C.

Somewhat surprisingly, the retentions of alkane solutes failed to correlate with stationary-phase molecular weight. The plots for n-hexane and n-octane are provided as examples in Figures 15 and 16: the data describe near-horizontal lines, i.e., fail to reflect solvent M.

Relative Retentions and Retention Indices. As a result of the above, the retention indices of probe-solutes, which are taken relative to n-alkanes, fail to correlate with inverse M. The data for the solutes of Figures 11-14 are shown in Figures 17-20. This is unfortunate, since retention indices can be taken directly from strip-chart recordings. However, capacity factors, which have the same advantage, can be used instead. Thus, one need in fact ensure only that the flow rate, temperature, and weight percent liquid loading of stationary phase are the same from one column to another, and then calculate the capacity factors of the probe-solutes methyl ethyl ketone, acetylacetone, butyronitrile, and valeronitrile. The data should regress linearly against inverse molecular weight since, if the specific retention volumes do so, then of course the capacity-factor data must also.

Application to Fractionated R-45M. An example of application of the findings of Phase I of the Contract are provided in Table 55, which lists the number-average molecular weights of each of the R-45M fractions that were calculated with the nomograph shown in Figure 10; the data are also plotted in Figure 21. The upper limit of accuracy of the method appears to be ca. 4000 Da, which is quite satisfactory since the number-average molecular weight of R-45M prepolymer rarely exceeds 2000 Da. The determination of R-45M M_n by inverse GC thus appears to be at hand.

TABLE 55. Number-Average Molecular Weights, M_n/Da, of Indicated Fractions of X-25LM R-45M Calculated from Nomographic Regression Shown in Figure 10 and Retention Data Listed in Tables 34-51

Fraction	V_g^o/cm^3 g^{-1}	M_n/Da
1A	810.4	902.
1B	780.5	1036.
2A	723.7	1444.
2B	711.1	1583.
3A	659.5	2607.
3B	629.3	4194.
4A	630.7	4078.
4B	628.5	4262.
5A	560.6	-
Bulk	706.6	1639.

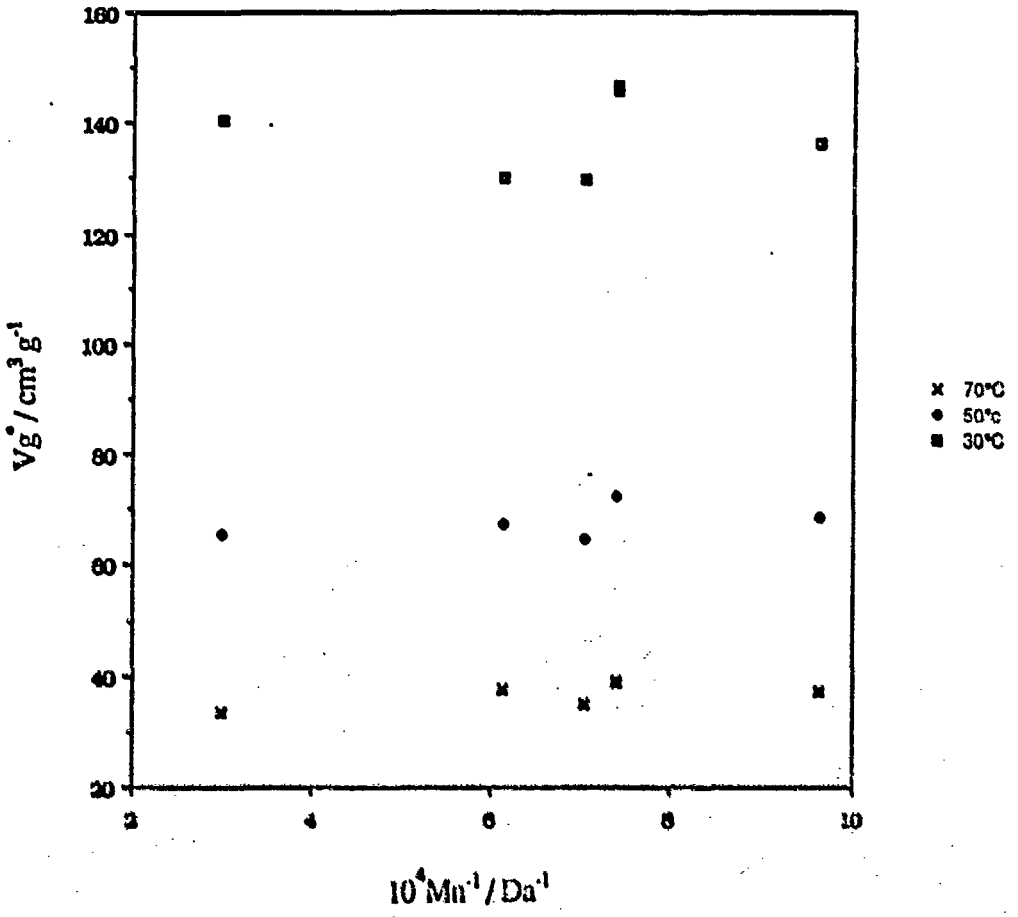

FIGURE 15. As in Figure 11; n-hexane solute at 30, 50, and 70°C.

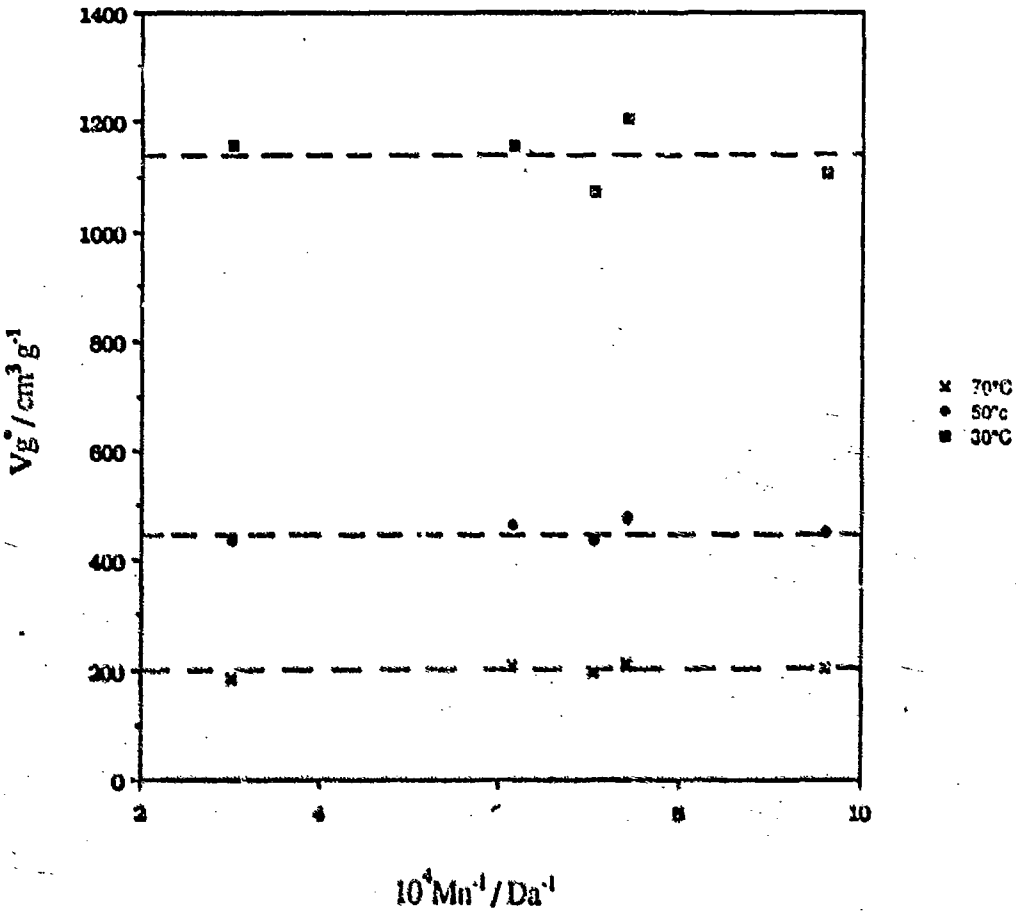

FIGURE 16. As in Figure 11; n-octane solute at 30, 50, and 70°C.

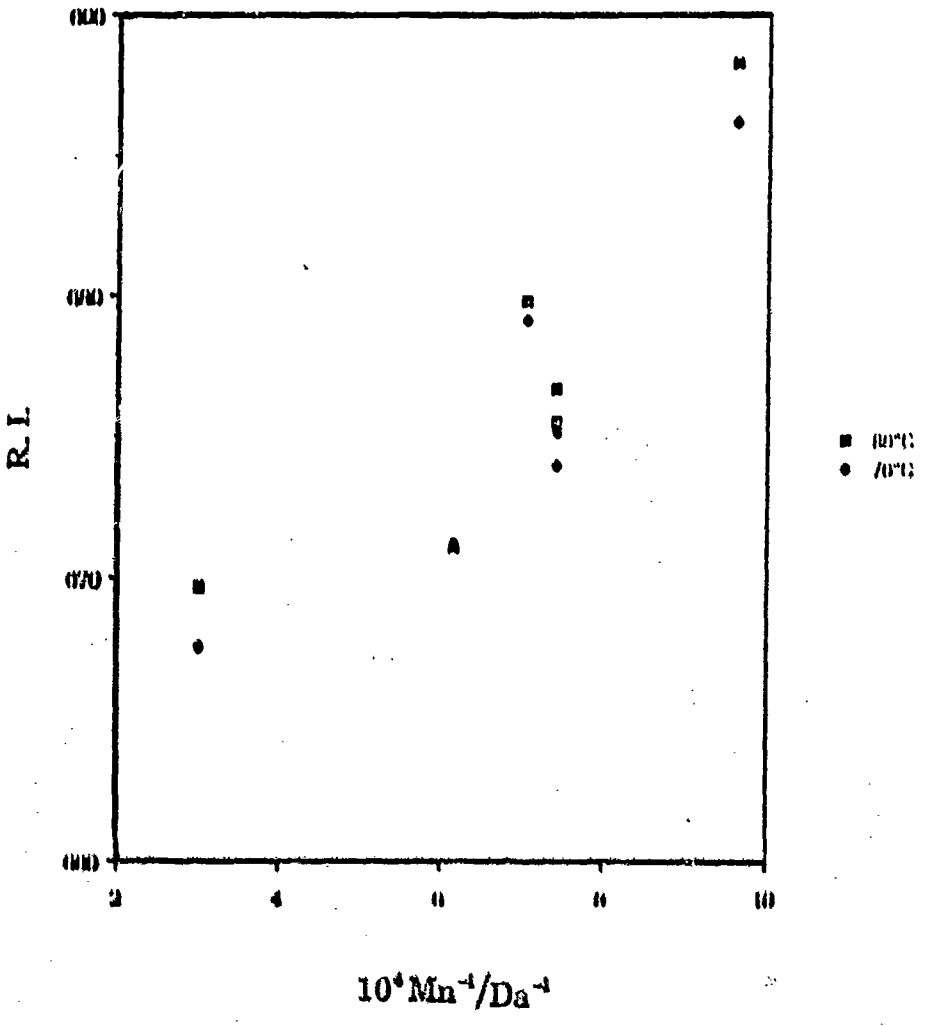

FIGURE 17. Plots of retention indices of methyl ethyl ketone solute against inverse molecular weight of R-45M standard stationary phases at indicated temperatures.

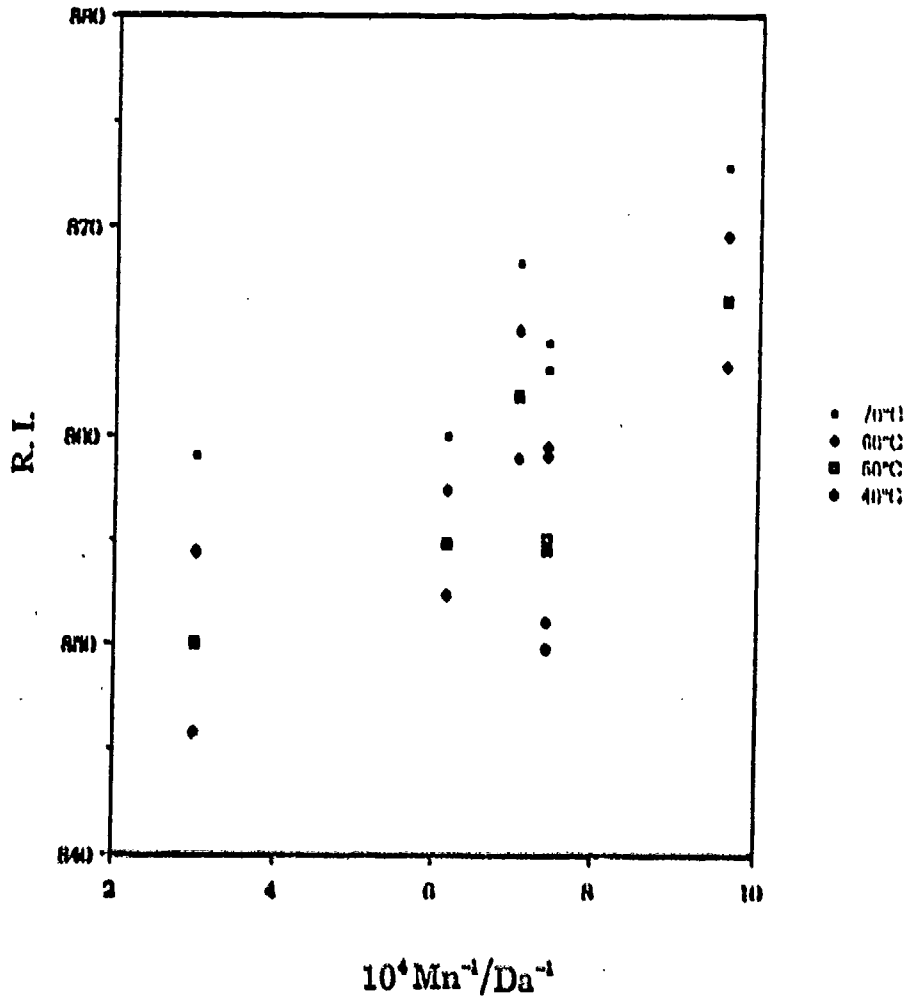

FIGURE 18. As in Figure 17; acetylacetone solute.

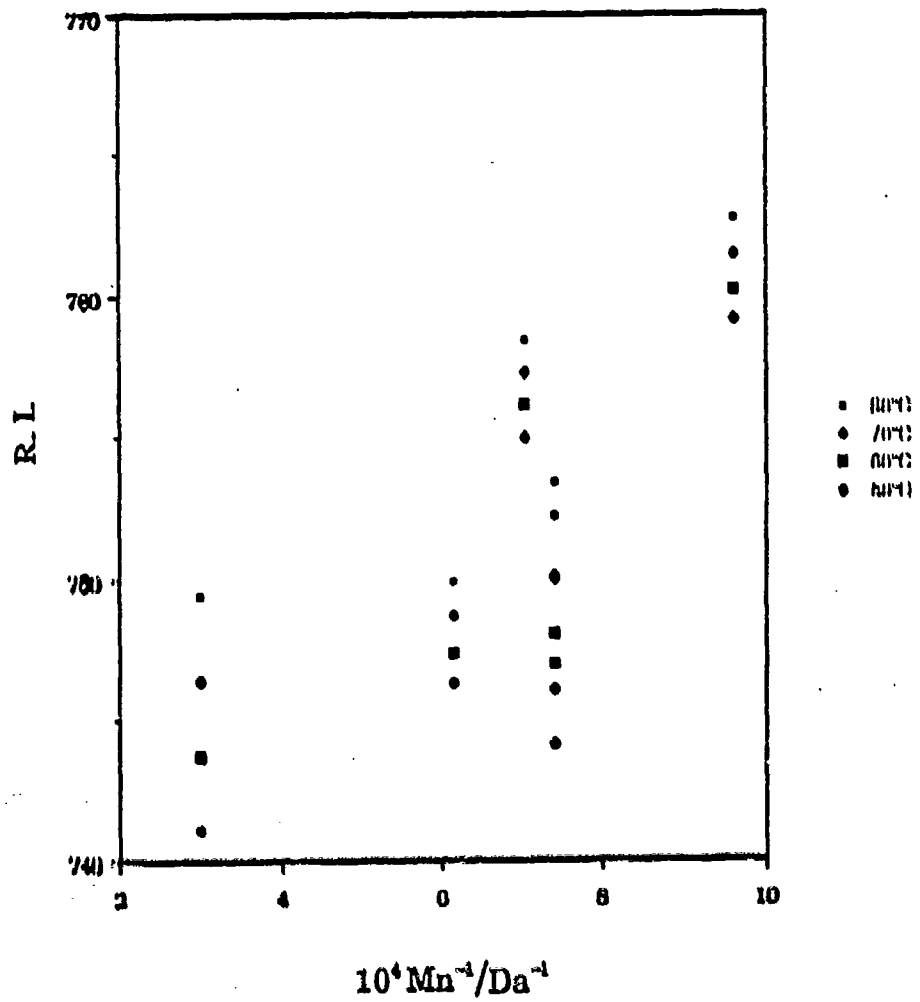

FIGURE 19. As in Figure 17; butyronitrile solute.

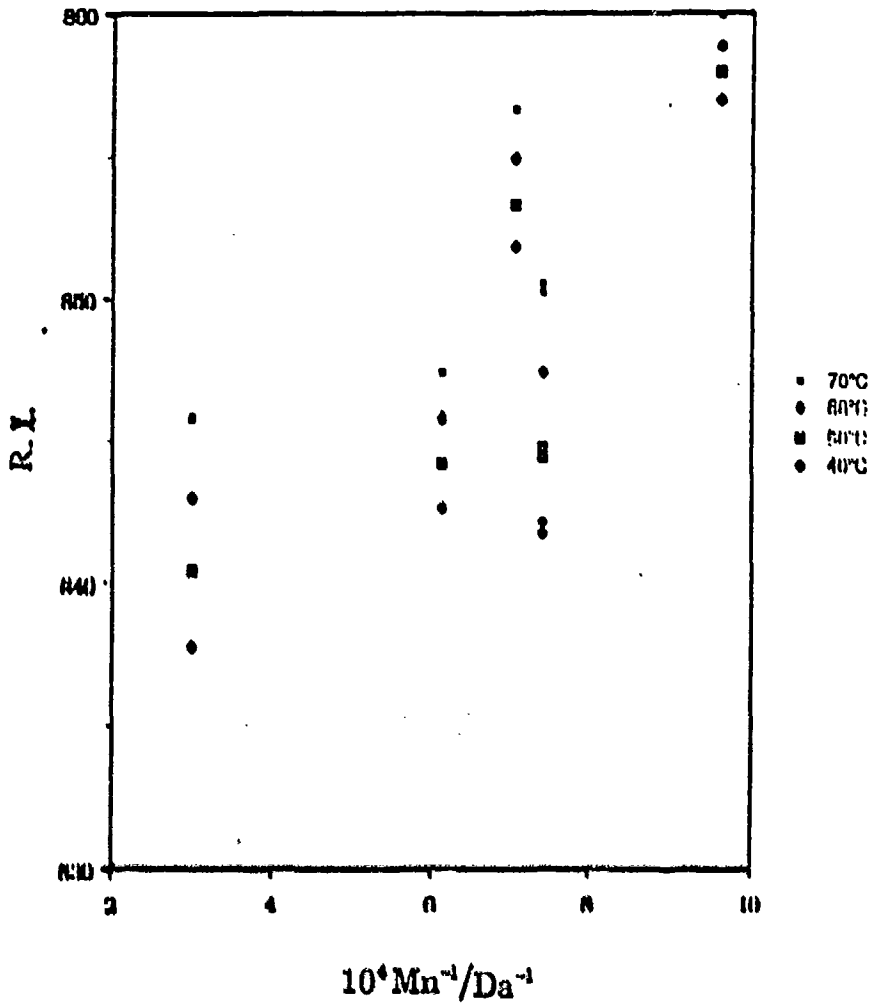

FIGURE 20. As in Figure 17; valeronitrile solute.

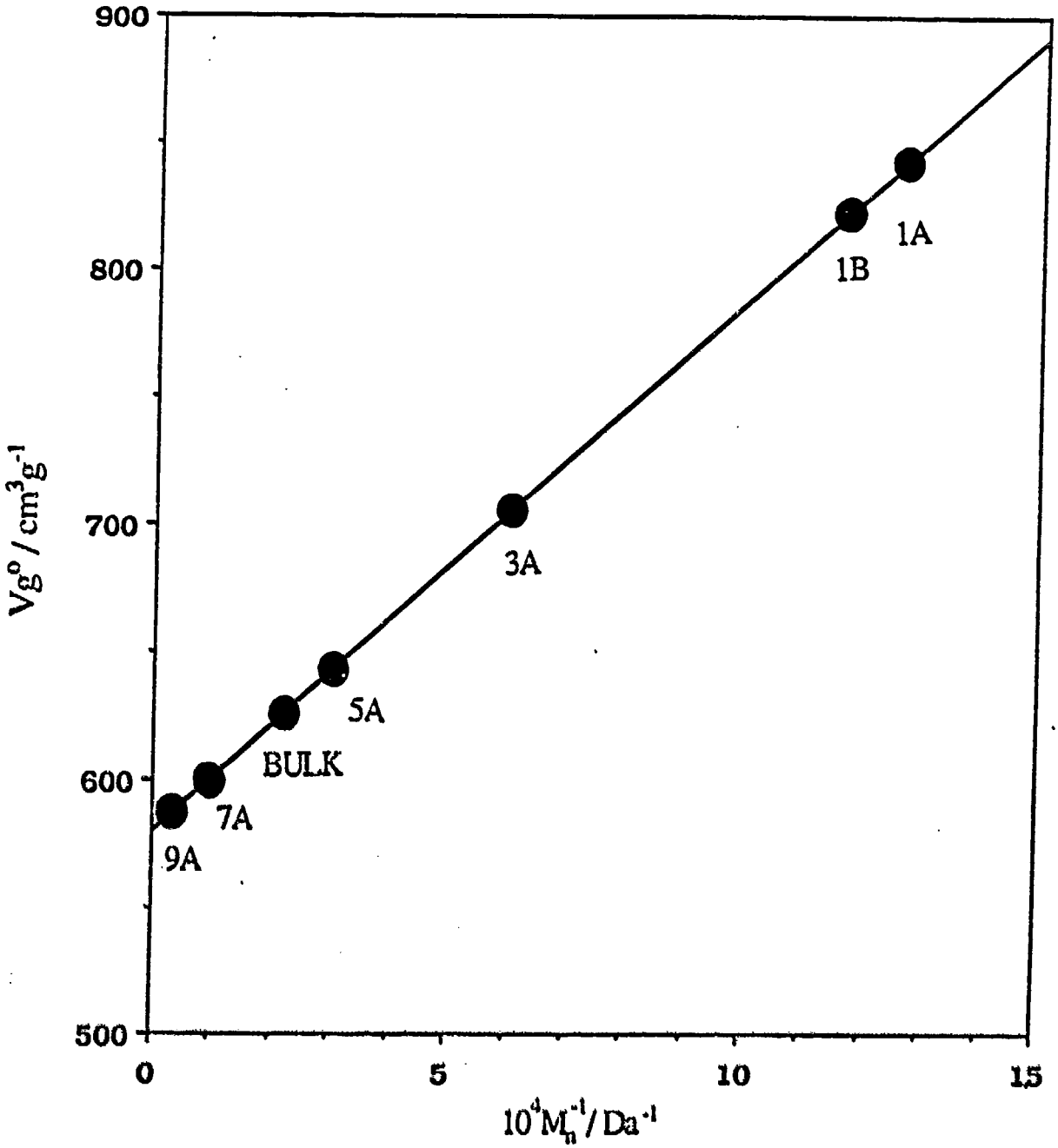

FIGURE 21. Nomographic determination of M_n of fractions 1A-10A of bulk 25LM R-45M calculated from the respective V_g^o and the linear regression shown in Figure 10 and Table 54.

Phase II, Task 1. Wet-Chemical/Instrumental Determination of Absolute Hydroxyl Content

"Standard" Lot of R-45M. The supply of ARCO Poly bd X-25LM had at this point been exhausted. In addition, the ARCO Division responsible for R-45M was sold and a new firm, Sartomer, came into being during the previous Phase of this work. (As of this writing, Sartomer has since been purchased by the French oil and chemicals firm, Elf Aquitaine.) As a result, and because we could not obtain any fresh supplies of ARCO X-25LM, the "standard" lot of R-45M was changed to Sartomer R20LM, with the assurance from Sartomer personnel that the material was in every way identical to Poly bd X-20LM batches formerly manufactured by ARCO. (In fact, this turned out not to be so, as described below.) It was therefore necessary to repeat virtually all of Phase I with the new Sartomer "standard" lot of prepolymer.

Gel-Permeation Chromatography of Bulk R-45M. The GPC traces of bulk ARCO (upper) and Sartomer lots of supposed-equivalent "20LM" are presented in Figure 22. A vertical line drawn through the peak-maximum of the former clearly does not pass through that of the latter. An appreciable amount of the Sartomer material appears in fact to be of substantially lower molecular weight than the ARCO version. The peaks are of about equal asymmetry, however, that is, there is a broad "front" (left side) and a relatively sharp "tail" (right side) to each.

Inverse GC Retentions with Bulk R-45M. The gas-chromatographic specific retention volumes, and van't Hoff slopes, intercepts, and least-squares correlation coefficients of all probe-solutes with the ARCO and Sartomer materials at 30-80°C are presented in Tables 56-65 below. The former data (Tables 56,57), obtained in the previous Phase of the Contract, obviously contrast sharply with those found for the Sartomer material (Tables 58-65) (see also later).

Solvent Fractionation Patterns of Bulk R-45M. The fractionation pattern obtained with iso-propyl alcohol/benzene with the Sartomer R20LM sample is shown in Figure 23, while, for comparison, that obtained for ARCO X-25LM is shown in Figure 24. The results were really quite startling: fully three-fourths of the Sartomer material was extracted in the first two extractions; indeed, two-thirds of the prepolymer was extracted in the first extraction with iso-propyl alcohol. Thus, the average molecular weight of the Sartomer material must be very substantially lower than, for example, ARCO X-25LM; cf. Figure 24. In the latter, only a third of the R-45M was taken up in the first fraction, the remaining two-thirds being distributed roughly equally between fractions 2-5. Shown also for comparison in Figures 25-27 are the extraction bar graph data obtained for Sartomer Lots 40, 42B, and ACH V004. These three bulk Sartomer materials appear to be similar to one another; however, there are notable differences in the amounts extracted for the last fraction, 6A. For example, Lots 40 and ACH V004 each give 15-16% w/w material for the last fraction, while that of Lot 42B is half this amount, ca. 8%. The patterns are also somewhat similar to ARCO X-25LM, but differ quite substantially from Sartomer R20LM.

Molecular-Weight Characterization of Fractions of "Standard" R-45M. Following fractionation of the new "standard", Sartomer R20LM, we proceeded to determine and compare the number-average molecular weight of each fraction by inverse GC, by density measurements, and by GPC.

Inverse GC Determination of Fraction Molecular Weights. It was found in previous work that the retentions of particular solutes, at specified temperatures, correlated well with R-45M stationary-phase molecular weight. The solutes were methyl ethyl ketone at 70-80°C, butyronitrile at 50-80°C, and valeronitrile and acetylacetone at 40-70°C. The corresponding nomographic equations are given below in Table 66. The retentions of these solutes with each of the Sartomer R20LM R-45M fractions are then

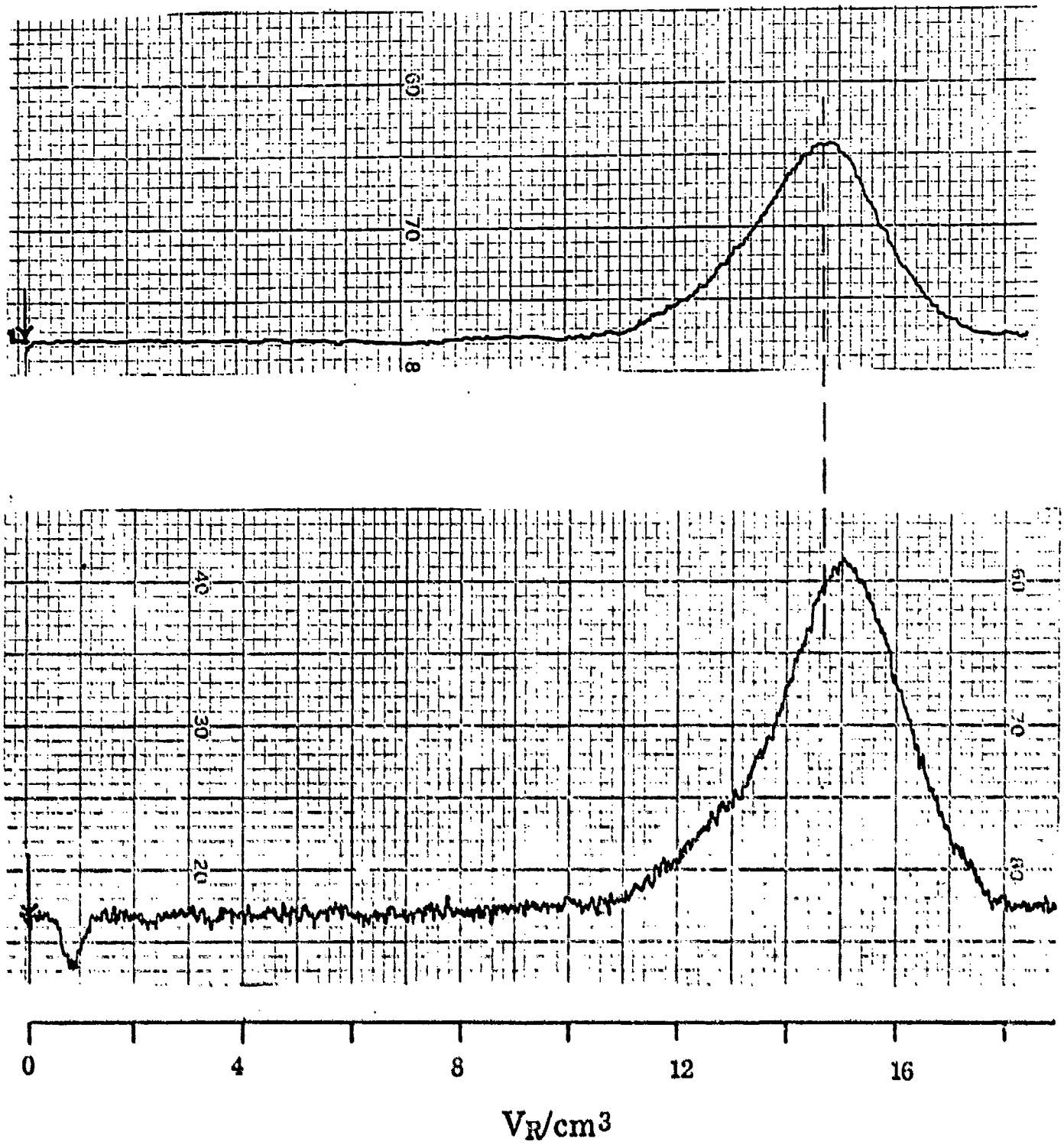

FIGURE 22. GPC traces of ARCO (upper) and Sartomer versions of 20LM R-45M.

TABLE 56. Smoothed (van't Hoff) Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ for Listed Probe Solutes at Indicated Temperatures with ARCO Poly bd X-20LM R-45M

	$V_g^o/cm^3\ g^{-1}$					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	49.91	36.77	27.61	21.09	16.36	12.88
n-Hexane	146.7	101.8	72.27	52.37	38.67	29.05
n-Heptane	421.5	276.0	185.5	127.7	89.85	64.49
n-Octane	1206.	744.6	473.6	309.6	207.4	142.2
3-Methylpentane	118.8	84.14	60.87	44.90	33.72	25.73
2,3-Dimethyl-pentane	297.5	201.0	139.1	98.44	71.08	52.28
3-Methylhexane	316.6	211.9	145.4	102.0	73.11	53.38
3-Methylheptane	873.6	552.3	359.2	239.8	163.9	114.4
1-Hexene	147.0	102.5	73.11	53.21	39.45	29.75
1-Heptene	420.6	276.9	187.0	129.4	91.41	65.88
1-Octene	1195.	740.6	472.8	310.0	208.4	143.2
Benzene	470.8	318.1	220.2	155.8	112.5	82.78
Toluene	1424.	906.6	593.7	398.8	274.2	192.6
Ethylbenzene	3383.	2080.	1318.	858.6	573.3	391.7
o-Xylene	5087.	3070.	1912.	1225.	805.5	542.4
p-Xylene	3935.	2392.	1500.	967.0	639.7	433.1
Cyclohexane	336.7	230.2	161.1	115.2	84.04	62.39
Methylcyclo-hexane	605.9	401.6	273.1	190.0	135.1	97.86
Tetrahydrofuran	460.0	306.6	209.5	146.5	104.6	76.10
Thiophene	579.3	388.5	267.0	187.7	134.7	98.46
Acetone	108.7	77.53	56.46	41.91	31.66	24.30
Methyl Ethyl Ketone	299.8	202.7	140.4	99.40	71.81	52.84
Methyl Propyl Ketone	743.4	478.6	316.6	214.7	148.9	105.5
Methyl Butyl Ketone	2115.	1290.	810.9	524.2	347.6	236.0
Acetylacetone	1964.	1234.	797.8	530.0	360.0	250.1
Methylene Chloride	130.6	93.09	67.75	50.26	37.93	29.09
Chloroform	364.7	245.7	169.6	119.7	86.26	63.31
1-Chloropentane	983.3	627.9	412.1	277.4	191.0	134.4
n-Butyronitrile	632.7	415.8	280.5	193.7	136.7	98.41
n-Valeronitrile	1837.	1138.	726.0	475.8	319.7	219.6

TABLE 57. Slopes m, Intercepts b, and Linear Regression Correlation Coefficients r for van't Hoff Plots of Ln V_g^o of Listed Probe-Solutes of Table 56 Against $10^3\ T^{-1}$ with Bulk ARCO Poly bd X-20LM R-45M

Probe Solute	m	- b	r
n-Pentane	2.901	5.659	0.9997_8
n-Hexane	3.467	6.448	0.9998_4
n-Heptane	4.020	7.216	0.9998_5
n-Octane	4.577	8.004	0.9998_7
3-Methylpentane	3.276	6.028	0.9997_7
2,3-Dimethylpentane	3.723	6.586	0.9998_0
3-Methylhexane	3.812	6.816	0.9997_2
3-Methylheptane	4.352	7.585	0.9997_5
1-Hexene	3.421	6.293	0.9997_1
1-Heptene	3.970	7.053	0.9998_2
1-Octene	4.542	7.898	0.9999_4
Benzene	3.722	6.123	0.9997_5
Toluene	4.283	6.869	0.9998_3
Ethylbenzene	4.617	7.102	0.9999_3
o-Xylene	4.793	7.275	0.9999_4
p-Xylene	4.725	7.308	0.9999_0
Cyclohexane	3.609	6.087	0.9997_8
Methylcyclohexane	3.904	6.470	0.9998_1
Tetrahydrofuran	3.852	6.576	0.9999_9
Thiophene	3.795	6.155	0.9998_0
Acetone	3.208	5.894	0.9998_8
Methyl Ethyl Ketone	3.717	6.558	0.9999_8
Methyl Propyl Ketone	4.182	7.183	0.9999_8
Methyl Butyl Ketone	4.696	7.833	0.9999_7
Acetylacetone	4.412	6.971	0.9999_2
Methylene Chloride	3.215	5.735	0.9999_3
Chloroform	3.749	6.468	0.9999_0
1-Chloropentane	4.262	7.169	0.9998_6
n-Butyronitrile	3.984	6.693	0.9999_7
n-Valeronitrile	4.548	7.487	0.9999_1

TABLE 58. Smoothed (van't Hoff) Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ for Listed Probe Solutes at Indicated Temperatures with Sartomer R20LM R-45M

	$V_g^o/cm^3\ g^{-1}$					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	39.54	29.99	23.15	18.14	14.42	11.62
n-Hexane	117.0	83.61	61.01	45.37	34.33	26.39
n-Heptane	336.5	227.0	156.9	110.8	79.93	58.72
n-Octane	957.7	609.5	398.9	267.8	184.0	129.2
3-Methylpentane	95.83	69.38	51.25	38.54	29.48	22.89
2,3-Dimethyl-pentane	239.1	165.3	116.9	84.38	62.09	46.49
3-Methylhexane	255.2	174.6	122.3	87.53	63.87	47.44
3-Methylheptane	701.4	453.6	301.4	205.2	142.9	101.6
1-Hexene	121.0	86.32	62.87	46.67	35.25	27.05
1-Heptene	343.4	232.1	160.7	113.7	82.13	60.42
1-Octene	966.9	617.3	405.2	272.8	187.9	132.2
Benzene	430.7	292.4	203.3	144.5	104.7	77.33
Toluene	1289.	825.0	542.9	366.3	252.9	178.3
Ethylbenzene	3050.	1892.	1209.	793.7	533.9	367.3
o-Xylene	4689.	2843.	1778.	1144.	755.0	510.2
p-Xylene	3557.	2181.	1378.	895.4	596.5	406.6
Cyclohexane	278.3	194.2	138.6	101.0	74.91	56.52
Methylcyclo-hexane	495.9	336.1	233.3	165.6	119.9	88.39
Tetrahydrofuran	447.6	301.3	207.9	146.7	105.6	77.44
Thiophene	553.8	372.2	256.4	180.6	129.9	95.14
Acetone	115.6	82.74	60.49	45.06	34.12	26.28
Methyl Ethyl Ketone	307.8	209.4	145.9	103.9	75.45	55.79
Methyl Propyl Ketone	751.0	487.0	324.3	221.3	154.4	110.0
Methyl Butyl Ketone	2132.	1305.	823.9	534.6	355.7	242.2
Acetylacetone	2062.	1288.	828.7	547.3	370.3	256.2
Methylene Chloride	132.7	94.19	68.27	50.44	37.94	29.00
Chloroform	371.5	248.9	170.9	120.0	86.08	62.89
1-Chloropentane	881.7	569.5	377.9	257.1	178.8	127.0
n-Butyronitrile	721.4	469.1	313.3	214.4	150.0	107.1
n-Valeronitrile	2006.	1242.	791.7	518.6	348.2	239.2
1,2-Dimethoxy-ethane	621.1	402.6	268.1	183.0	127.7	90.90

TABLE 59. Slopes m, Intercepts b, and Linear Regression Correlation Coefficients r for van't Hoff Plots of Ln V_g^o of Listed Probe-Solutes of Table 58 Against 10^3 T^{-1} with Sartomer R20LM R-45M

Probe Solute	m	- b	r
n-Pentane	2.622	4.973	0.9988_6
n-Hexane	3.188	5.756	0.9992_6
n-Heptane	3.738	6.513	0.9994_0
n-Octane	4.289	7.285	0.9994_8
3-Methylpentane	3.066	5.552	0.9996_7
2,3-Dimethylpentane	3.507	6.090	0.9997_4
3-Methylhexane	3.603	6.342	0.9997_7
3-Methylheptane	4.137	7.095	0.9997_8
1-Hexene	3.208	5.785	0.9993_8
1-Heptene	3.720	6.433	0.9994_6
1-Octene	4.260	7.179	0.9995_1
Benzene	3.677	6.064	0.9996_1
Toluene	4.236	6.811	0.9998_0
Ethylbenzene	4.532	6.927	0.9999_9
o-Xylene	4.750	7.215	0.9999_9
p-Xylene	4.044	7.142	0.9999_7
Cyclohexane	3.413	5.630	0.9996_8
Methylcyclohexane	3.693	5.974	0.9997_4
Tetrahydrofuran	3.756	6.287	0.9999_2
Thiophene	3.771	6.124	0.9998_6
Acetone	3.171	5.709	0.9999_2
Methyl Ethyl Ketone	3.657	6.334	0.9999_5
Methyl Propyl Ketone	4.113	6.947	0.9998_8
Methyl Butyl Ketone	4.657	7.696	0.9998_6
Acetylacetone	4.466	7.099	0.9999_0
Methylene Chloride	3.257	5.856	0.9997_7
Chloroform	3.803	6.626	0.9998_2
1-Chloropentane	4.149	6.906	0.9997_8
n-Butyronitrile	4.085	6.894	0.9999_4
n-Valeronitrile	4.553	7.416	0.9999_4
1,2-Dimethoxy-ethane	4.114	7.141	0.9999_8

TABLE 60. Smoothed (van't Hoff) Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ for Listed Probe Solutes at Indicated Temperatures with Sartomer Lot 40 R-45M

	$V_g^o/cm^3\ g^{-1}$					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	52.54	38.59	28.89	22.01	17.04	13.38
n-Hexane	157.2	108.7	76.95	55.59	40.93	30.66
n-Heptane	456.4	298.3	200.2	137.6	96.70	69.32
n-Octane	1321.	812.4	514.8	335.3	224.0	153.0
3-Methylpentane	128.4	90.14	64.67	47.33	35.27	26.73
2,3-Dimethyl-pentane	322.5	216.9	149.4	105.3	75.75	55.51
3-Methylhexane	345.2	229.3	156.2	109.0	77.56	56.30
3-Methylheptane	961.9	603.4	389.5	258.2	175.3	121.6
1-Hexene	155.7	108.1	76.77	55.65	41.10	30.88
1-Heptene	451.7	296.0	199.2	137.2	96.61	69.39
1-Octene	1288.	797.4	508.5	333.2	223.8	153.7
Benzene	481.9	324.0	223.2	157.3	113.1	82.85
Toluene	1478.	934.5	607.9	405.7	277.3	193.6
Ethylbenzene	3665.	2216.	1382.	886.6	583.8	393.6
o-Xylene	5562.	3302.	2024.	1278.	828.5	550.6
p-Xylene	4203.	2530.	1571.	1004.	658.5	442.3
Cyclohexane	361.2	246.0	171.6	122.3	88.92	65.82
Methylcyclo-hexane	654.4	432.1	292.7	203.0	143.8	103.9
Tetrahydrofuran	409.3	273.8	187.7	131.7	94.30	68.81
Thiophene	584.4	391.1	268.4	188.3	134.9	98.51
Acetone	92.83	65.83	47.69	35.22	26.48	20.23
Methyl Ethyl Ketone	258.1	174.4	120.8	85.52	61.77	45.45
Methyl Propyl Ketone	649.7	417.8	276.0	187.0	129.6	91.68
Methyl Butyl Ketone	1878.	1139.	71[illegible]5	458.4	302.6	204.5
Acetylacetone	1761.	1095.	701.2	461.3	310.9	214.3
Methylene Chloride	124.9	89.02	64.78	48.04	36.26	27.80
Chloroform	341.1	231.3	160.7	114.1	82.66	60.98
1-Chloropentane	996.7	637.2	418.7	282.2	194.6	137.1
n-Butyronitrile	525.5	345.1	232.6	160.5	113.2	81.43
n-Valeronitrile	1514.	942.1	603.7	397.3	267.9	184.7
1,2-Dimethoxy-ethane	555.0	356.0	234.7	158.7	109.7	77.51

TABLE 61. Slopes m, Intercepts b, and Linear Regression Correlation Coefficients r for van't Hoff Plots of Ln V_g^o of Listed Probe-Solutes of Table 60 Against $10^3\ T^{-1}$ with Sartomer Lot 40 R-45M

Probe Solute	m	- b	r
n-Pentane	2.930	5.702	0.9998_7
n-Hexane	3.500	6.488	0.9999_5
n-Heptane	4.035	7.188	0.9999_4
n-Octane	4.615	8.038	0.9999_7
3-Methylpentane	3.361	6.231	0.9999_4
2,3-Dimethylpentane	3.767	6.651	0.9998_4
3-Methylhexane	3.883	6.964	0.9999_3
3-Methylheptane	4.427	7.736	0.9999_4
1-Hexene	3.464	6.380	0.9999_8
1-Heptene	4.011	7.118	0.9999_6
1-Octene	4.552	7.854	0.9999_5
Benzene	3.770	6.258	0.9999_5
Toluene	4.352	7.058	0.9999_6
Ethylbenzene	4.778	7.553	0.9999_6
o-Xylene	4.952	7.711	0.9998_8
p-Xylene	4.821	7.559	0.9999_6
Cyclohexane	3.645	6.135	0.9999_2
Methylcyclohexane	3.940	6.513	0.9999_4
Tetrahydrofuran	3.818	6.580	0.9999_6
Thiophene	3.812	6.205	0.9999_4
Acetone	3.263	6.231	0.9998_8
Methyl Ethyl Ketone	3.718	6.712	0.9999_1
Methyl Propyl Ketone	4.193	7.354	0.9999_3
Methyl Butyl Ketone	4.748	8.124	0.9999_8
Acetylacetone	4.509	7.401	0.9999_5
Methylene Chloride	3.218	5.786	0.9999_4
Chloroform	3.686	6.327	0.9999_7
1-Chloropentane	4.248	7.107	0.9999_2
n-Butyronitrile	3.993	6.906	0.9999_7
n-Valeronitrile	4.504	7.536	0.9999_9
1,2-Dimethoxy-ethane	4.215	7.585	0.9999_5

TABLE 62. Smoothed (van't Hoff) Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ for Listed Probe Solutes at Indicated Temperatures with Sartomer Lot 42B R-45M

	$V_g^o/cm^3\ g^{-1}$					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	52.80	38.81	29.07	22.16	17.16	13.49
n-Hexane	157.4	109.0	77.21	55.83	41.14	30.84
n-Heptane	459.7	299.3	200.1	137.0	95.96	68.56
n-Octane	1312.	808.7	513.6	335.2	224.3	153.5
3-Methylpentane	128.1	90.19	64.90	47.63	35.60	27.05
2,3-Dimethyl-pentane	320.7	215.9	148.9	105.0	75.58	55.42
3-Methylhexane	343.1	228.6	156.2	109.2	77.93	56.69
3-Methylheptane	953.5	599.8	388.3	258.1	175.6	122.1
1-Hexene	156.0	108.3	76.96	55.81	41.24	30.99
1-Heptene	450.5	295.4	198.9	137.1	96.57	69.39
1-Octene	1279.	793.0	506.3	332.1	223.2	153.5
Benzene	482.0	324.8	224.2	158.3	114.1	83.72
Toluene	1472.	933.1	608.4	407.1	278.8	195.1
Ethylbenzene	3598.	2190.	1375.	887.2	587.4	398.1
o-Xylene	5355.	3211.	1987.	1266.	827.6	554.3
p-Xylene	4096.	2483.	1553.	999.1	659.4	445.6
Cyclohexane	361.8	246.4	171.9	122.5	89.06	65.92
Methylcyclo-hexane	653.2	431.3	292.3	202.7	143.6	103.8
Tetrahydrofuran	411.2	275.5	189.3	132.9	95.32	69.66
Thiophene	584.9	391.7	268.9	188.8	135.3	98.84
Acetone	96.49	66.35	49.22	36.24	27.16	20.69
Methyl Ethyl Ketone	263.7	177.8	122.8	86.75	62.53	45.92
Methyl Propyl Ketone	658.4	423.0	279.3	189.0	130.9	92.56
Methyl Butyl Ketone	1876.	1142.	716.8	462.7	306.4	207.7
Acetylacetone	1754.	1096.	705.1	465.7	315.2	218.0
Methylene Chloride	126.3	90.04	65.55	48.64	36.72	28.17
Chloroform	348.9	235.7	163.2	115.5	83.39	61.34
1-Chloropentane	1007.	641.6	420.5	282.7	194.5	136.6
n-Butyronitrile	534.3	350.9	236.5	163.2	115.1	82.80
n-Valeronitrile	1530.	953.2	611.7	403.1	272.2	187.9
1,2-Dimethoxy-ethane	560.9	359.3	236.6	159.7	110.3	77.84

TABLE 63. Slopes m, Intercepts b, and Linear Regression Correlation Coefficients r for van't Hoff Plots of Ln V_g^o of Listed Probe-Solutes of Table 62 Against 10^3 T^{-1} with Sartomer Lot 42B R-45M

Probe Solute	m	-b	r
n-Pentane	2.922	5.674	0.9999_3
n-Hexane	3.490	6.455	0.9999_2
n-Heptane	4.074	7.309	0.9999_0
n-Octane	4.593	7.973	0.9999_1
3-Methylpentane	3.330	6.131	0.9998_6
2,3-Dimethylpentane	3.759	6.629	0.9998_5
3-Methylhexane	3.855	6.879	0.9998_6
3-Methylheptane	4.400	7.653	0.9998_8
1-Hexene	3.460	6.363	0.9999_2
1-Heptene	4.005	7.102	0.9999_2
1-Octene	4.541	7.824	0.9999_3
Benzene	3.748	6.186	0.9999_5
Toluene	4.327	6.979	0.9999_3
Ethylbenzene	4.714	7.361	0.9999_9
o-Xylene	4.856	7.433	0.9999_9
p-Xylene	4.750	7.350	0.9999_9
Cyclohexane	3.646	6.135	0.9998_9
Methylcyclohexane	3.939	6.512	0.9998_9
Tetrahydrofuran	3.801	6.521	0.9999_7
Thiophene	3.807	6.186	0.9999_1
Acetone	3.297	6.306	0.9999_7
Methyl Ethyl Ketone	3.742	6.771	0.9999_7
Methyl Propyl Ketone	4.201	7.367	0.9999_8
Methyl Butyl Ketone	4.712	8.006	0.9999_9
Acetylacetone	4.465	7.258	0.9999_7
Methylene Chloride	3.213	5.759	0.9998_9
Chloroform	3.722	6.423	0.9999_0
1-Chloropentane	4.276	7.190	0.9999_2
n-Butyronitrile	3.992	6.888	0.9999_4
n-Valeronitrile	4.490	7.478	0.9999_8
1,2-Dimethoxy-ethane	4.229	7.620	0.9999_5

TABLE 64. Smoothed (van't Hoff) Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ for Listed Probe Solutes at Indicated Temperatures with Sartomer Lot ACH V004 R-45M

	$V_g^o/cm^3\ g^{-1}$					
	30°C	40°C	50°C	60°C	70°C	80°C
n-Pentane	52.59	38.64	28.94	22.06	17.08	13.42
n-Hexane	156.5	108.3	76.67	55.42	40.82	30.60
n-Heptane	454.8	296.8	198.8	136.5	95.74	68.53
n-Octane	1304.	803.5	510.2	332.9	222.7	152.4
3-Methylpentane	127.5	89.74	64.53	47.33	35.35	26.84
2,3-Dimethyl-pentane	317.9	214.2	147.9	104.4	75.19	55.18
3-Methylhexane	341.3	227.4	155.3	108.6	77.49	56.37
3-Methylheptane	946.6	595.9	386.0	256.7	174.8	121.6
1-Hexene	155.2	107.6	76.27	55.20	40.71	30.54
1-Heptene	447.6	293.3	197.2	135.8	95.61	68.65
1-Octene	1279.	790.6	503.5	329.4	220.9	151.6
Benzene	479.0	322.0	221.8	156.3	112.4	82.34
Toluene	1461.	925.3	602.8	402.9	275.7	192.7
Ethylbenzene	3594.	2180.	1363.	877.3	579.2	391.5
o-Xylene	5497.	3252.	1988.	1252.	809.4	536.6
p-Xylene	4193.	2512.	1553.	988.7	646.1	432.5
Cyclohexane	359.5	244.4	170.2	121.1	87.91	64.98
Methylcyclo-hexane	650.3	428.7	290.1	200.9	142.1	102.6
Tetrahydrofuran	422.9	281.0	191.5	133.5	95.11	69.05
Thiophene	577.1	386.0	264.7	185.6	132.9	97.01
Acetone	94.38	67.25	48.94	36.29	27.39	21.01
Methyl Ethyl Ketone	264.0	177.8	122.8	86.65	62.41	45.80
Methyl Propyl Ketone	663.6	425.2	280.1	189.2	130.7	92.24
Methyl Butyl Ketone	1905.	1154.	721.0	463.4	305.6	206.3
Acetylacetone	1780.	1103.	704.2	461.8	310.4	213.4
Methylene Chloride	124.5	88.51	64.29	47.60	35.87	27.46
Chloroform	343.6	231.6	160.0	113.0	81.41	59.77
1-Chloropentane	1005.	637.4	416.0	278.6	190.9	133.7
n-Butyronitrile	538.1	351.6	235.8	162.0	113.8	81.52
n-Valeronitrile	1561.	963.3	612.4	400.1	267.9	183.5
1,2-Dimethoxy-ethane	564.8	361.8	238.2	160.8	111.1	78.34

TABLE 65. Slopes m, Intercepts b, and Linear Regression Correlation Coefficients r for van't Hoff Plots of Ln V_g^o of Listed Probe-Solutes of Table 64 Against 10^3 T^{-1} with Sartomer Lot ACH V004 R$_g$-45M

Probe Solute	m	- b	r
n-Pentane	2.925	5.686	0.9997_1
n-Hexane	3.495	6.475	0.9998_8
n-Heptane	4.052	7.248	0.9998_7
n-Octane	4.596	7.987	0.9999_1
3-Methylpentane	3.337	6.161	0.9998_5
2,3-Dimethylpentane	3.750	6.608	0.9999_1
3-Methylhexane	3.856	6.887	0.9999_0
3-Methylheptane	4.394	7.641	0.9999_1
1-Hexene	3.481	6.439	0.9999_2
1-Heptene	4.015	7.139	0.9999_4
1-Octene	4.567	7.910	0.9999_3
Benzene	3.770	6.265	0.9999_6
Toluene	4.337	7.021	0.9999_5
Ethylbenzene	4.747	7.471	0.9999_8
o-Xylene	4.982	7.823	0.9999_9
p-Xylene	4.863	7.703	0.9999_8
Cyclohexane	3.663	6.198	0.9999_4
Methylcyclohexane	3.955	6.568	0.9999_4
Tetrahydrofuran	3.880	6.753	0.9998_8
Thiophene	3.818	6.236	0.9999_8
Acetone	3.217	6.065	0.9997_9
Methyl Ethyl Ketone	3.751	6.797	0.9999_3
Methyl Propyl Ketone	4.225	7.440	0.9999_7
Methyl Butyl Ketone	4.759	8.148	0.9999_6
Acetylacetone	4.542	7.498	0.9999_9
Methylene Chloride	3.236	5.850	0.9999_8
Chloroform	3.745	6.514	0.9999_8
1-Chloropentane	4.318	7.331	0.9999_8
n-Butyronitrile	4.041	7.041	0.9999_9
n-Valeronitrile	4.584	7.767	0.9999_9
1,2-Dimethoxy-ethane	4.230	7.616	0.9999_7

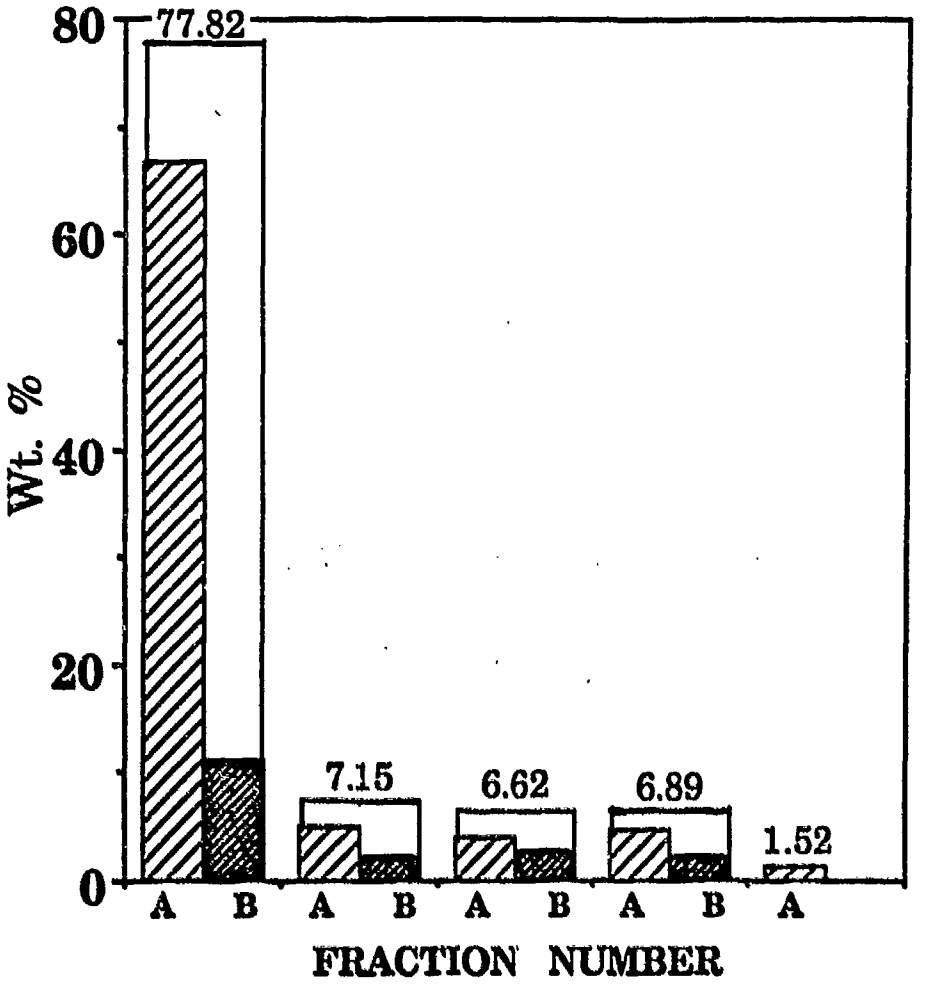

FIGURE 23. Fractionation pattern obtained for Sartomer R20LM R-45M.

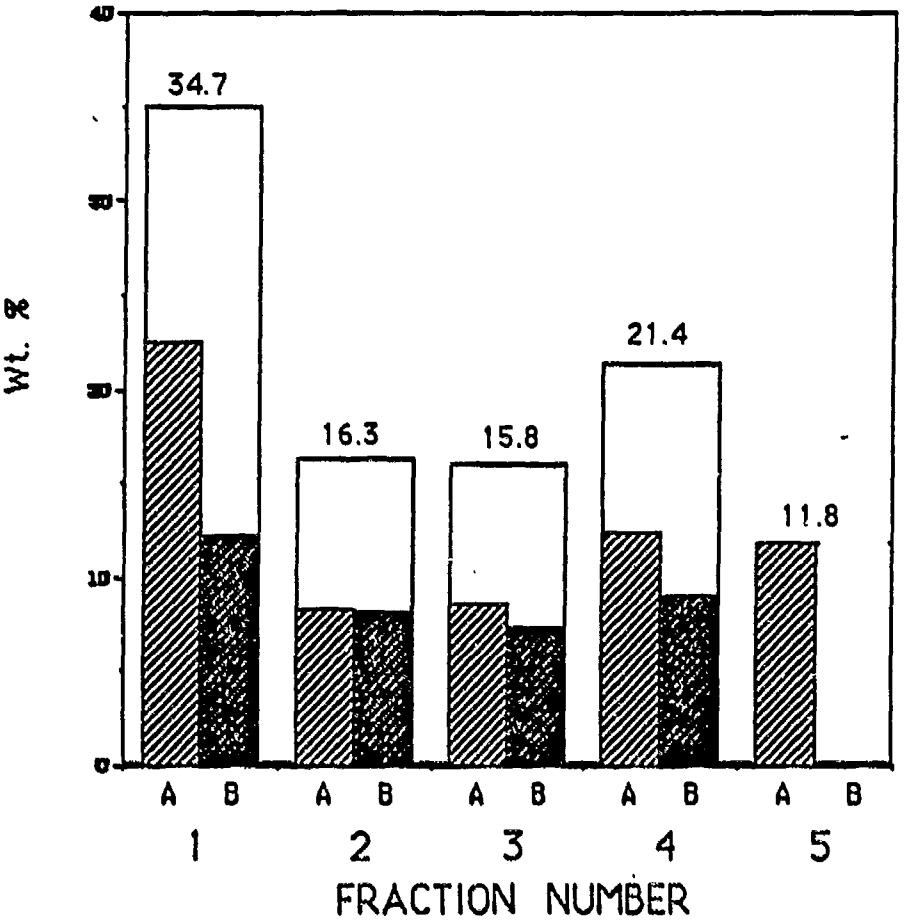

FIGURE 24. Fractionation pattern obtained for ARCO X-25LM R-45M.

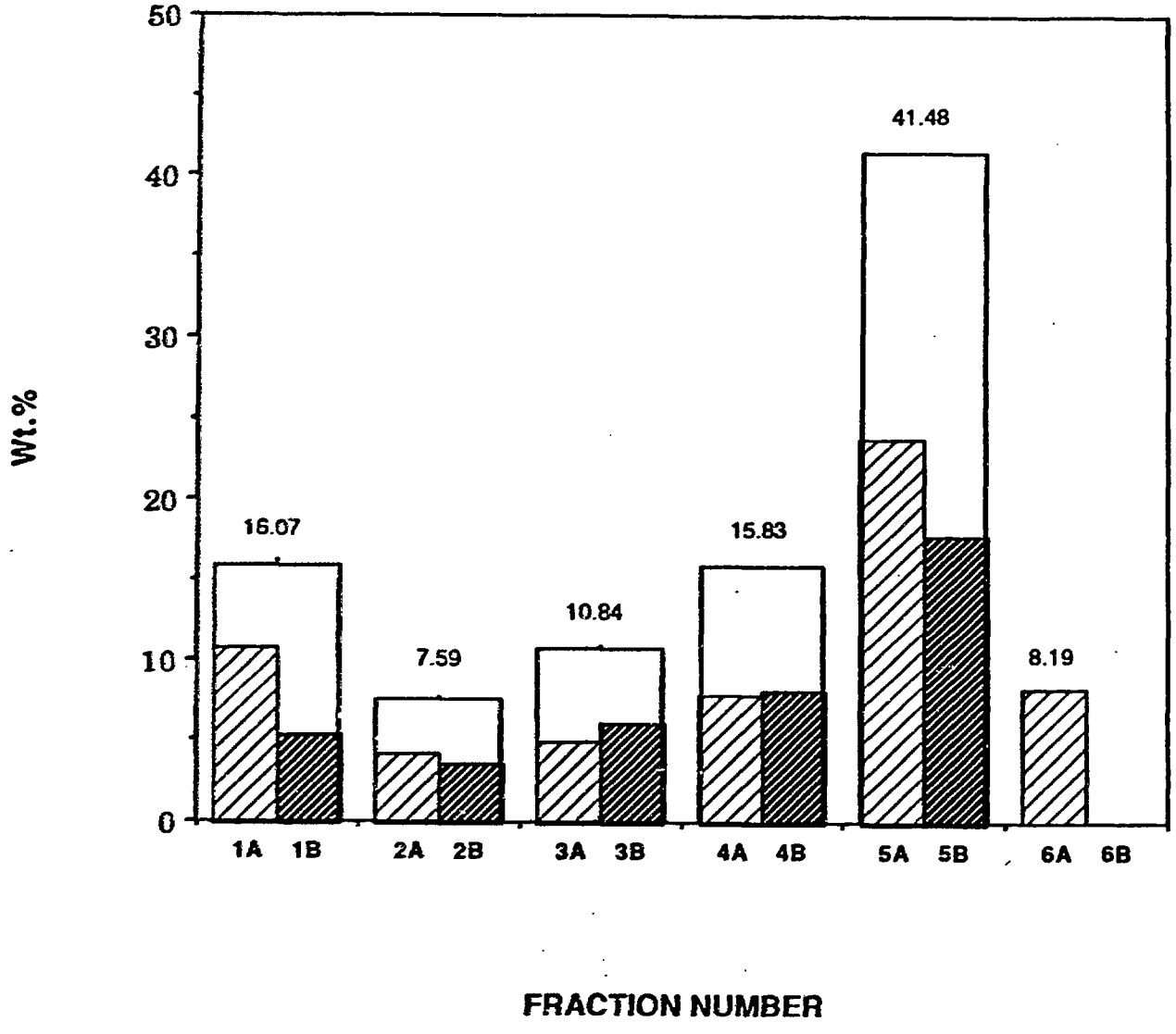

FIGURE 25. Solvent fractionation pattern obtained for Sartomer Lot 40 R-45M.

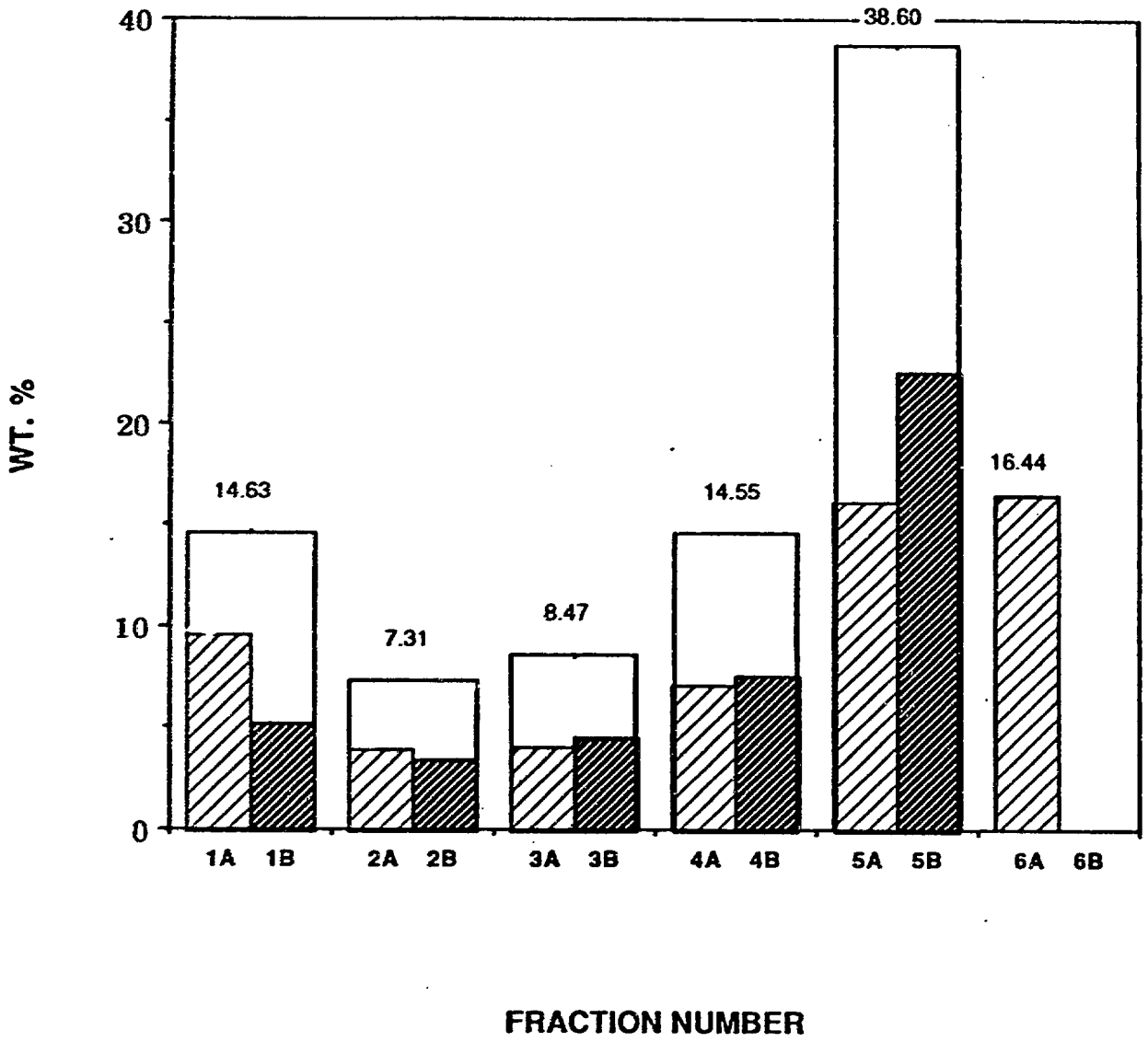

FIGURE 26. As in Figure 25; Sartomer Lot 42B R-45M.

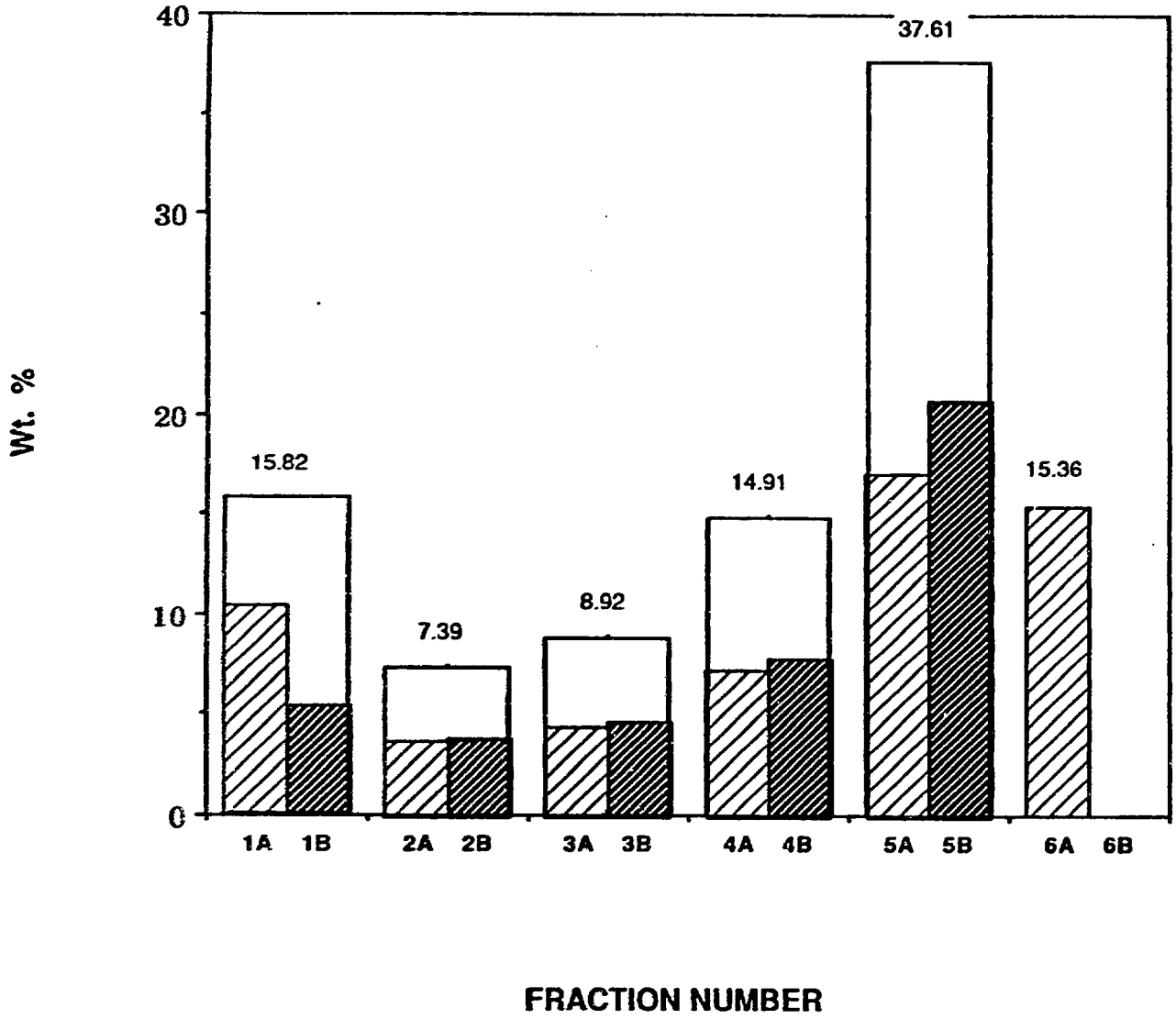

FIGURE 27. As in Figure 25; Sartomer Lot ACH V004 R-45M.

TABLE 66. Constants and Linear Least-Squares Regression Correlation Coefficients r of Nomographic Equations Relating Solute Retention to R-45M Stationary-Phase Number-Average Molecular Weight: $V_g^o = b + 10^4 m/M_n$

Solute	T/°C	b	m	r
Methyl Ethyl Ketone	70	51.082	2.7571	0.984
	80	36.447	2.1922	0.986
Acetylacetone	40	1028.4	29.767	0.985
	50	643.48	21.267	0.989
	60	414.33	15.312	0.984
	70	273.61	11.150	0.977
Butyronitrile	50	223.47	8.5264	0.995
	60	150.18	6.2046	0.997
	70	103.35	4.5705	0.990
	80	72.658	3.4187	0.980
Valeronitrile	40	930.06	30.384	0.980
	50	579.74	20.677	0.999
	60	371.62	14.354	0.994
	70	244.48	10.137	0.976

presented in Tables 67-75. The relations were used with the retentions to calculate the molecular weight of each fraction. The results are provided in Tables 76-84, and are grouped both by solute as well as by temperature. The data are also shown graphically in Figure 28. The various probe-solutes give quite good agreement for the molecular weights of the fractions, which were found to range from ca. 900 Da (1A) to ca. 12000 Da (5A). The bulk averaged ca. 1100 Da.

Density Determination of Fraction Molecular Weights. It will be recalled from previous work that the density of R-45M was found to correlate with its number-average molecular weight. Shown in Figure 29 is the regression of density against fraction number; the error bars correspond to $\pm$ 0.002 g cm^{-3}, the estimated error on the measurements. As shown, within these limits one could draw virtually any line-shape, that is, the density data were insufficiently accurate to permit quantitative determination of the fraction molecular weights. (The density observed for fraction 4A is clearly very discrepant.) Even so, density measurements are nevertheless an excellent way of detecting gross differences between bulk lots of R-45M.

TABLE 67. Smoothed (van't Hoff) Specific Retention Volumes V_g^o/cm^3 g^{-1} and Linear Least-Squares Correlation Coefficients r for Listed Probe Solutes at Indicated Temperatures with Fraction 1A of Sartomer R20LM R-45M

	V_g^o/cm^3 g^{-1}					
	40°C	50°C	60°C	70°C	80°C	r
Methyl Ethyl Ketone				79.43	58.88	(1.0)
Acetylacetone	1323.	861.1	575.2	393.4		0.9999_8
Butyronitrile		315.5	219.8	156.5	113.5	0.9999_9
Valeronitrile	1246.	804.0	532.5	361.3		0.9999_8

TABLE 68. As in Table 67; Fraction 1B

	$V_g^o/cm^3\ g^{-1}$					
	40°C	50°C	60°C	70°C	80°C	r
Methyl Ethyl Ketone				78.40	58.00	(1.0)
Acetylacetone	1299.	843.1	561.5	383.0		0.9998_4
Butyronitrile		307.9	214.6	152.8	110.9	0.9999_5
Valeronitrile	1229.	790.6	522.2	353.4		0.9999_3

TABLE 69. As in Table 67; Fraction 2A

	$V_g^o/cm^3\ g^{-1}$					
	40°C	50°C	60°C	70°C	80°C	r
Methyl Ethyl Ketone				68.37	51.36	(1.0)
Acetylacetone	1213.	776.5	510.7	344.1		0.9999_3
Butyronitrile		273.0	189.0	133.7	94.48	0.9997_7
Valeronitrile	1111.	706.8	462.1	309.7		0.9999_6

TABLE 70. As in Table 67; Fraction 2B

	$V_g^o/cm^3\ g^{-1}$					
	40°C	50°C	60°C	70°C	80°C	r
Methyl Ethyl Ketone				67.20	49.53	(1.0)
Acetylacetone	1181.	754.0	494.7	332.6		0.9999_8
Butyronitrile		269.3	184.7	129.5	92.63	0.9998_2
Valeronitrile	1085.	688.2	448.5	299.6		0.9999_9

TABLE 71. As in Table 67; Fraction 3A

	$V_g^o/cm^3\ g^{-1}$					
	40°C	50°C	60°C	70°C	80°C	r
Methyl Ethyl Ketone				61.97	45.84	(1.0)
Acetylacetone	1085.	694.7	456.7	307.6		0.9999_8
Butyronitrile		240.3	165.8	117.0	84.15	0.9999_8
Valeronitrile	958.1	611.4	400.8	269.3		0.9999_9

TABLE 72. As in Table 67; Fraction 3B

	$V_g^o/cm^3\ g^{-1}$					
	40°C	50°C	60°C	70°C	80°C	r
Methyl Ethyl Ketone				60.96	44.52	(1.0)
Acetylacetone	1069.	685.8	452.0	305.2		0.9999_8
Butyronitrile		233.4	161.9	114.8	82.96	0.9999_8
Valeronitrile	944.3	604.6	397.5	267.9		0.9999_9

TABLE 73. As in Table 67; Fraction 4A

	$V_g^o/cm^3\ g^{-1}$					
	40°C	50°C	60°C	70°C	80°C	r
Methyl Ethyl Ketone				60.61	43.82	(1.0)
Acetylacetone	1074.	685.5	449.6	302.3		0.9999_9
Butyronitrile		237.0	163.0	114.6	82.24	0.9999_9
Valeronitrile	951.1	607.1	398.1	267.5		0.9999_2

TABLE 74. As in Table 67; Fraction 4B

	$V_g^o/cm^3\ g^{-1}$					
	40°C	50°C	60°C	70°C	80°C	r
Methyl Ethyl Ketone				56.87	42.44	(1.0)
Acetylacetone	995.4	638.5	420.6	283.9		0.9998_1
Butyronitrile		212.0	148.3	105.8	77.01	0.9999_4
Valeronitrile	872.6	555.9	363.9	244.1		0.9996_3

TABLE 75. As in Table 67; Fraction 5A

	$V_g^o/cm^3\ g^{-1}$					
	40°C	50°C	60°C	70°C	80°C	r
Methyl Ethyl Ketone				56.82	41.53	(1.0)
Acetylacetone	968.9	619.0	406.3	273.2		0.9999_6
Butyronitrile		211.7	147.2	104.5	75.66	0.9999_6
Valeronitrile	830.3	530.7	348.5	234.5		0.9998_9

TABLE 76. Number-Average Molecular Weights of Indicated Fractions of Sartomer R20LM R-45M Determined from Retentions of Methyl Ethyl Ketone Solute at 70-80°C

	M_n/Da		
Fraction	70°C	80°C	Ave.
1A	972.5	972.9	972.7
1B	1009.	1013.	1011.
2A	1576.	1463.	1520.
2B	1710.	1667.	1689.
3A	—	—	—
3B	—	—	—
4A	—	—	—
4B	—	—	—
5A	—	—	—
Bulk R20LM	1131.	1133.	1132.

TABLE 77. As in Table 76; Acetylacetone Solute at 40-70°C

	M_n/Da				
Fraction	40°C	50°C	60°C	70°C	Ave.
1A	1011.	977.2	951.7	930.8	967.7
1B	1099.	1065.	1040.	1020.	1056.
2A	1615.	1599.	1590.	1581.	1596.
2B	1956.	1925.	1906.	1889.	1919.
3A	5213.	4153.	3617.	3277.	4065.
3B	—	5028.	4071.	3532.	4210.
4A	6576.	5063.	4340.	3894.	4968.
4B	9023.	—	—	10800.	9912.
5A	11580.	—	—	12200.	11890.
Bulk R20LM	1147.	1148.	1152.	1153.	1150.

TABLE 78. As in Table 76; Butyronitrile Solute at 50-80°C

	M_n/Da				
Fraction	50°C	60°C	70°C	80°C	Ave.
1A	926.8	890.6	860.4	836.3	878.5
1B	1010.	962.5	923.7	893.2	947.4
2A	1723.	1598.	1505.	1435.	1565.
2B	1860.	1797.	1749.	1712.	1780.
3A	5082.	3964.	3356.	2974.	3844.
3B	—	5285.	4001.	3318.	4201.
4A	6315.	4826.	4047.	3567.	4689.
4B	7455.	—	—	7853.	7654.
5A	—	—	—	11410.	11410.
Bulk R20LM	949.2	966.2	979.8	992.6	972.0

TABLE 79. As in Table 76; Valeronitrile Solute at 40-70°C

	M_n/Da				
Fraction	40°C	50°C	60°C	70°C	Ave.
1A	961.3	922.1	892.1	867.7	910.8
1B	1016.	980.6	953.0	930.6	970.1
2A	1681.	1627.	1586.	1554.	1612.
2B	1958.	1907.	1868.	1837.	1893.
3A	—	—	—	4079.	4079.
3B	—	—	—	4332.	4332.
4A	—	—	5425.	4397.	4911.
4B	—	—	—	—	—
5A	—	—	13010.	—	13010.
Bulk R20LM	974.0	977.9	976.6	977.3	976.5

TABLE 80. Number-Average Molecular Weights of Fractions of Sartomer R20LM R-45M Determined from Retentions of Indicated Probe-Solutes at 40°C

	M_n/Da		
Fraction	Acetylacetone Solute	Valeronitrile Solute	Ave.
1A	1011.	961.3	986.2
1B	1099.	1016.	1058.
2A	1615.	1681.	1648.
2B	1956.	1958.	1957.
3A	5213.	—	5213.
3B	—	—	—
4A	6576.	—	6576.
4B	9023.	—	9023.
5A	11580.	—	11580.
Bulk R20LM	1147.	974.0	1061.

TABLE 81. As in Table 80; 50°C

Fraction	M_n/Da			
	Acetylacetone Solute	Butyronitrile Solute	Valeronitrile Solute	Ave.
1A	977.2	926.8	922.1	942.0
1B	1065.	1010.	980.6	1019.
2A	1599.	1723.	1627.	1650.
2B	1925.	1860.	1907.	1897.
3A	4153.	5082.	—	4618.
3B	5028.	—	—	5028.
4A	5063.	6315.	—	5689.
4B	—	7455.	—	7455.
5A	—	—	—	—
Bulk R20LM	1148.	949.2	1148.	1025.

TABLE 82. As in Table 80; 60°C

Fraction	M_n/Da			
	Acetylacetone Solute	Butyronitrile Solute	Valeronitrile Solute	Ave.
1A	951.7	890.6	892.1	911.5
1B	1040.	962.5	953.0	985.2
2A	1590.	1598.	1586.	1591.
2B	1906.	1797.	1868.	1857.
3A	3617.	3964.	—	3791.
3B	4071.	5285.	—	4678.
4A	4340.	4826.	5425.	4864.
4B	—	—	—	—
5A	—	—	13010.	13010.
Bulk R20LM	1152.	966.2	976.6	1032.

TABLE 83. As in Table 80; 70°C

Fraction	M_n/Da				
	Methyl Ethyl Ketone Solute	Acetylacetone Solute	Butyronitrile Solute	Valeronitrile Solute	Ave.
1A	972.5	930.8	860.4	867.7	907.9
1B	1009.	1020.	923.7	930.6	970.8
2A	1576.	1581.	1505.	1554.	1554.
2B	1710.	1889.	1749.	1837.	1796.
3A	—	3277.	3356.	4079.	3571.
3B	—	3532.	4001.	4332.	3955.
4A	—	3894.	4047.	4397.	4113.
4B	—	10800.	—	—	10800.
5A	—	12200.	—	—	12200.
Bulk R20LM	1131.	1153.	979.8	977.3	1065.

TABLE 84. As in Table 80; 80°C

Fraction	M_n/Da		
	Methyl Ethyl Ketone Solute	Butyronitrile Solute	Ave.
1A	972.9	836.3	904.6
1B	1013.	893.2	953.1
2A	1463.	1435.	1449.
2B	1667.	1712.	1690.
3A	—	2974.	2974.
3B	—	3318.	3318.
4A	—	3567.	3567.
4B	—	7853.	7853.
5A	—	11410.	11410.
Bulk R20LM	1133.	992.6	1063.

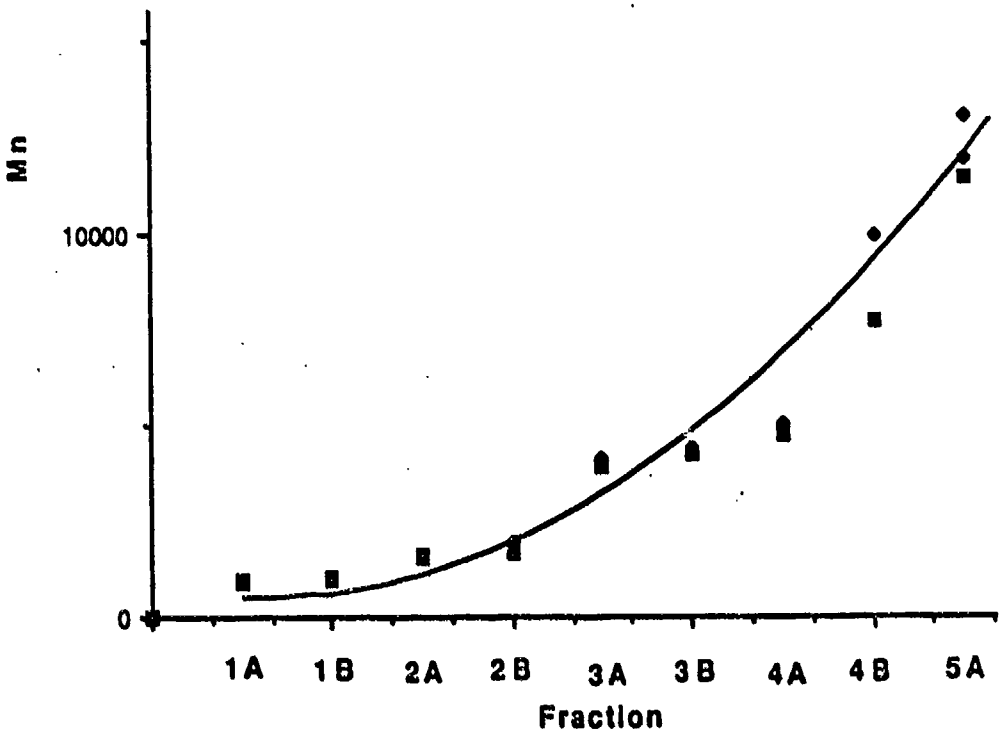

FIGURE 28. Number-average molecular weights of R-45M fractions from inverse GC data of Tables 80-84.

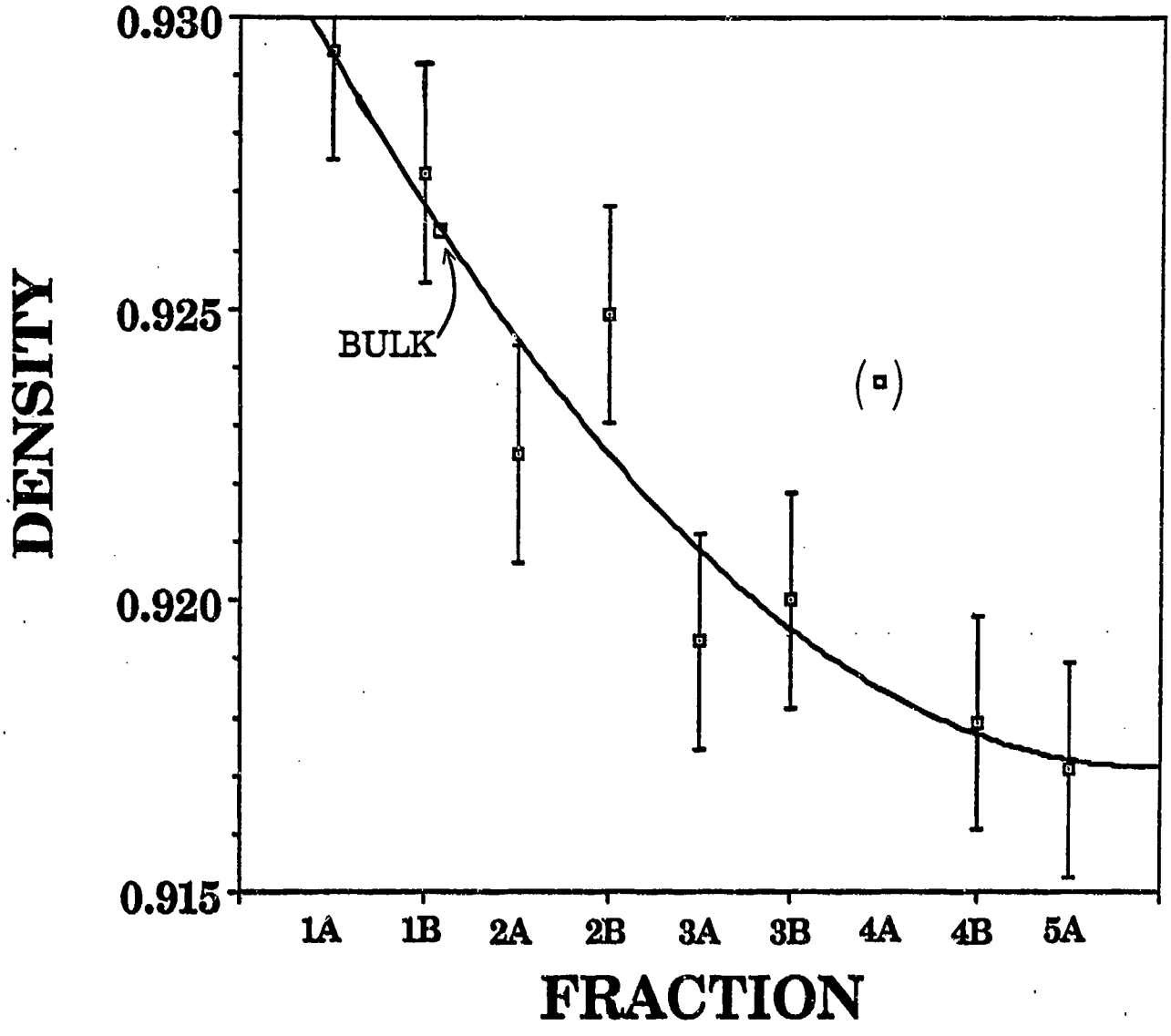

FIGURE 29. Regression of density against fraction molecular weight.

Gel-Permeation Chromatographic Determination of Fraction Molecular Weights. The GPC calibration plot of log M_n against V_R is shown in Figure 30, where the R-45M standards were the ARCO X series, described in previous work, and toluene. There is some scatter in the data; nevertheless, linear regression (r = 0.98) gave the equation: log $M_n = 6.405 - 0.222\ V_R$. The fraction molecular weights determined with this relation and their retention volumes are provided below in Table 85, where a comparison with the averages of the GC data is also made. There was some doubt about the GPC molecular weights of fractions 4A, 4B and 5A due to multiple peaks observed for each. Those for fractions 4A and 5A are shown in Figures 31 and 32 as illustrations. The remaining data are in reasonable agreement with those observed by inverse gas chromatography.

Overall, it was shown in this portion of the work that the inverse GC method does indeed offer a means of assessing the stationary-phase molecular weight. However, there is some temperature-dependence of the data, as shown in Tables 80-84. Greater accuracy is therefore gained when the molecular weights of lots of R-45M are calculated from the averages of those derived from the probe-solute retentions at several temperatures.

TABLE 85. Comparison of Inverse GC (Tables 80-84) and GPC Number-Average Molecular Weights for Indicated Fractions of Sartomer R20LM R-45M

	M_n/Da	
Fraction	GC	GPC
1A	932.4	940.2
1B	996.1	1067.
2A	1573.	1422.
2B	1787.	—
3A	3996.	—
3B	4206.	—
4A	4856.	(3925.)
4B	8783.	(4025.)
5A	12103.	—
Bulk R20LM	1058.	1247.

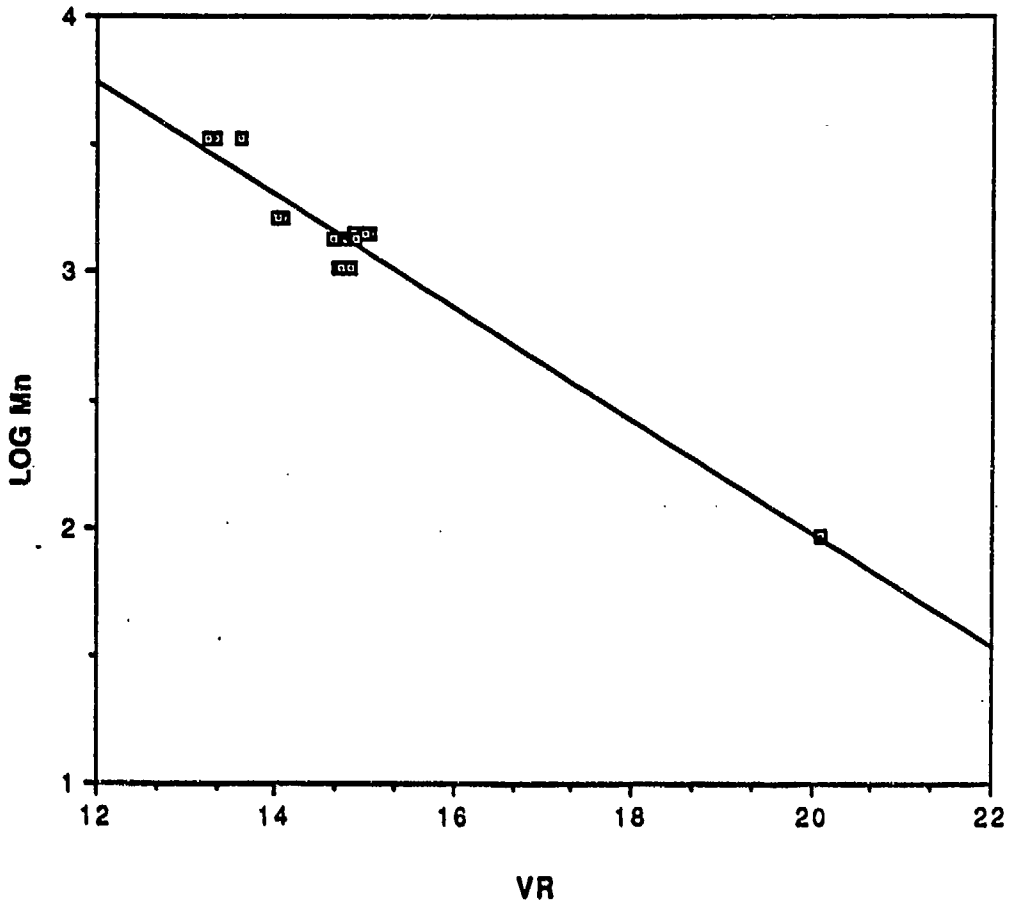

FIGURE 30. GPC nomograph of log M_n against V_R for ARCO R-45M standards and toluene.

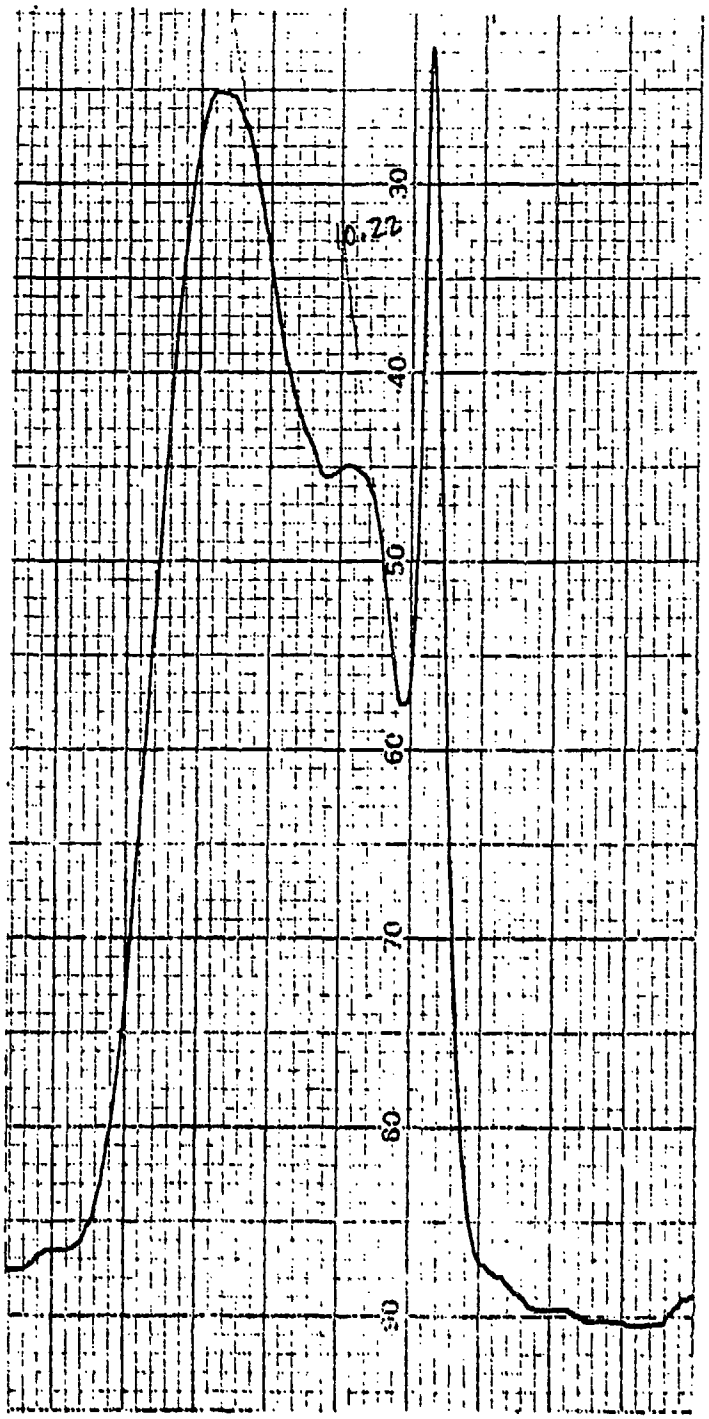

FIGURE 31. GPC pattern obtained for fraction 4A of Sartomer R20LM R-45M.

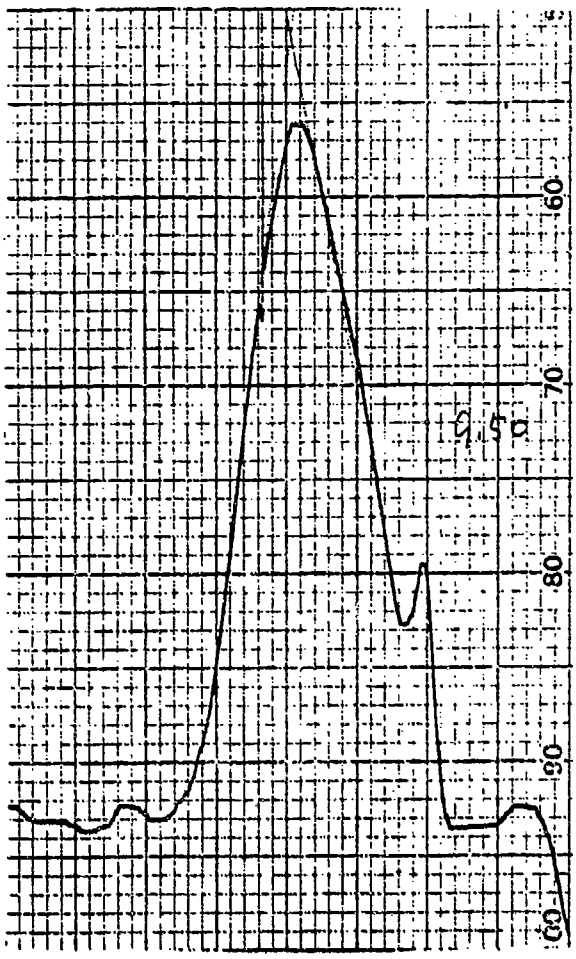

FIGURE 32. As in Figure 31; fraction 5A.

Fraction Hydroxyl Content. The concentrations used to define the hydroxyl-content nomograph constructed with the standard 6-undecanol are provided in Table 86. The values ranged from 20 up to 100 meq dm^{-3}. A plot of the results is then shown in Figure 33. The equation of the straight line is: $Y = 1.5566X + 14.63$; with a correlation coefficient of at least 0.999. The finite intercept is consistent with that found in previous work. That is, the method is applicable to hydroxyl values of no less than ca. 20 meq dm^{-3}.

As a test of the goodness of fit of the data, as well as the overall applicability of the method, the ARCO standards comprised of the "X" series, 10LM, 14LM, 20LM, 25LM, and 120HM, were also run. The reported (Hinney, et al., loc. cit.) and measured hydroxyl values are provided in Table 87. The agreement is reasonably satisfactory.

The hydroxyl contents of the Sartomer R20LM fractions, obtained as described above, as well as those of R-45M samples obtained later from AL, are reported in Table 88. The former data are shown plotted in Figure 34, and regress according to the relation: $Y = 0.02176X^2 - 0.4248X + 2.447$.

Phase II, Task 2. GLC Determination of Hydroxyl Content

Hydroxyl-Content Independence of Retentions of Molecular-Weight Probe Solutes. In seeking to establish a set of probe-solutes whose retentions are sensitive to hydroxyl content, molecular-weight effects must of course also be accounted for. That is, changes in M could be mistaken for changes in OH content unless a method can be derived that takes the former into consideration. As a corollary, the molecular-weight probe solutes should of course be independent of hydroxyl content, for the same reason. As it happened, three lots of R-45M were to hand with which these criteria could be evaluated for given sets of solutes.

Table 89 presents the retentions of the two most useful molecular-weight marker solutes, butyronitrile and valeronitrile, at the three best temperatures, 50-70°C, with three batches of R-45M, Lots 40, ACH V004, and 42B. Also given are the hydroxyl contents and molecular weights of the materials. (Recall that the solvent-extraction patterns of the materials, Figures 25-27, were nearly identical.) As shown, the retentions of the solutes at each temperature fall to within an experimental error of at worst ca. ± 1.5%. It is also fortunate that n-alkyl nitriles turn out to be useful as marker solutes, since homologous series behavior (e.g., regressions against carbon number) and the employment of retention indices thereby become possible (see later). There is in any event little question that the retentions of these solutes are dependent upon the solvent molecular weight, but are independent of the solvent hydroxyl content.

Further confirmation of the accuracy with which the nitriles reflect molecular weight is provided in Table 90, which gives the retentions of the solutes with the ARCO X series of standards. Also shown are the linear least-squares correlation coefficients, r, for the regressions of V_g^0 against Mn^{-1}, which should be straight lines. The correlations are exact at 50°C, although fall off somewhat at 70°C. Note also that the hydroxyl contents of the prepolymers run from 1.73 meq g^{-1} for X-10LM to 0.59 meq g^{-1} for X-120HM, that is, fall by a factor of 3, yet the retention/molecular-weight correlations still hold. That is, the retentions are dependent upon the molecular weight, but are independent of the hydroxyl content.

TABLE 86. Amounts of 6-Undecanol Standard Employed for FT-IR Nomographic Determination of Hydroxyl Content of Samples of R-45M

Hydroxyl Content/meq dm^{-3}	6-Undecanol Concentration/meq g^{-1}
19.994	47.8
38.894	73.7
58.886	104.2
81.347	141.9
99.767	170.8

TABLE 87. Test of Accuracy of FT-IR Nomographic Determination of Hydroxyl Content with ARCO "X" Series of R-45M

	Hydroxyl Content/meq g^{-1}	
Sample	Claimed	Found
X-10LM	1.75	1.69
X-14LM	1.43	1.36
X-20LM	1.39	1.39
X-25LM	1.19	1.12
X-120HM	0.60	0.57

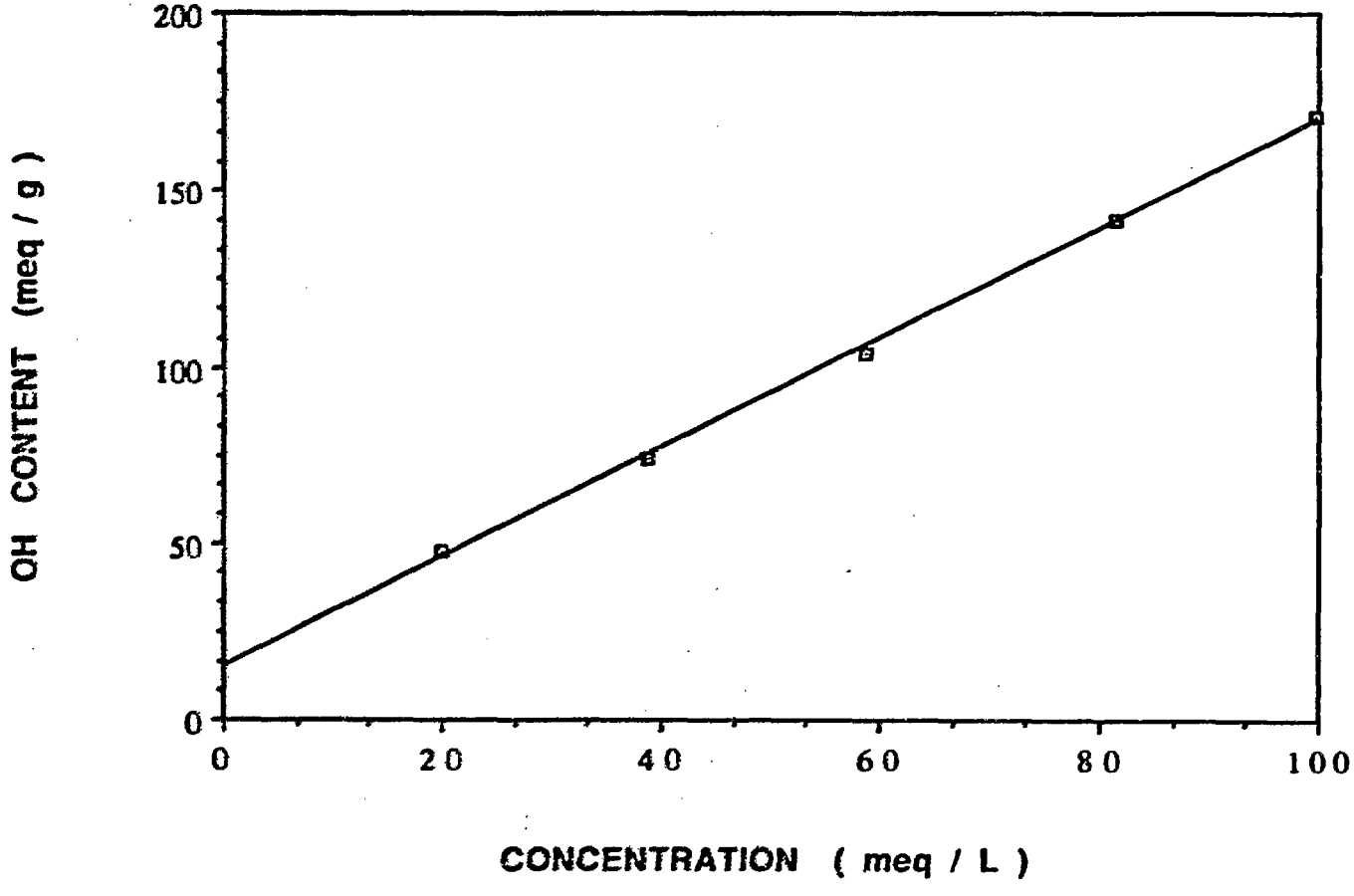

FIGURE 33. Hydroxyl-Content Nomograph Constructed from Data of Table 86.

TABLE 88. Hydroxyl Content of Bulk and Fractionated R-45M

A. Fractionated R-20LM

Sample	Hydroxyl Content/meq g^{-1}
1A	1.94
1B	1.97
2A	1.27
2B	-
3A	0.74
3B	0.69
4A	-
4B	0.62
5A	0.23
Bulk	1.73

B. Bulk R-45M

Lot 40	0.72
Lot 42B	1.19
Lot T002	1.10
Lot ACH V001	1.03
Lot ACH V004	0.96
Lot A812819	1.07

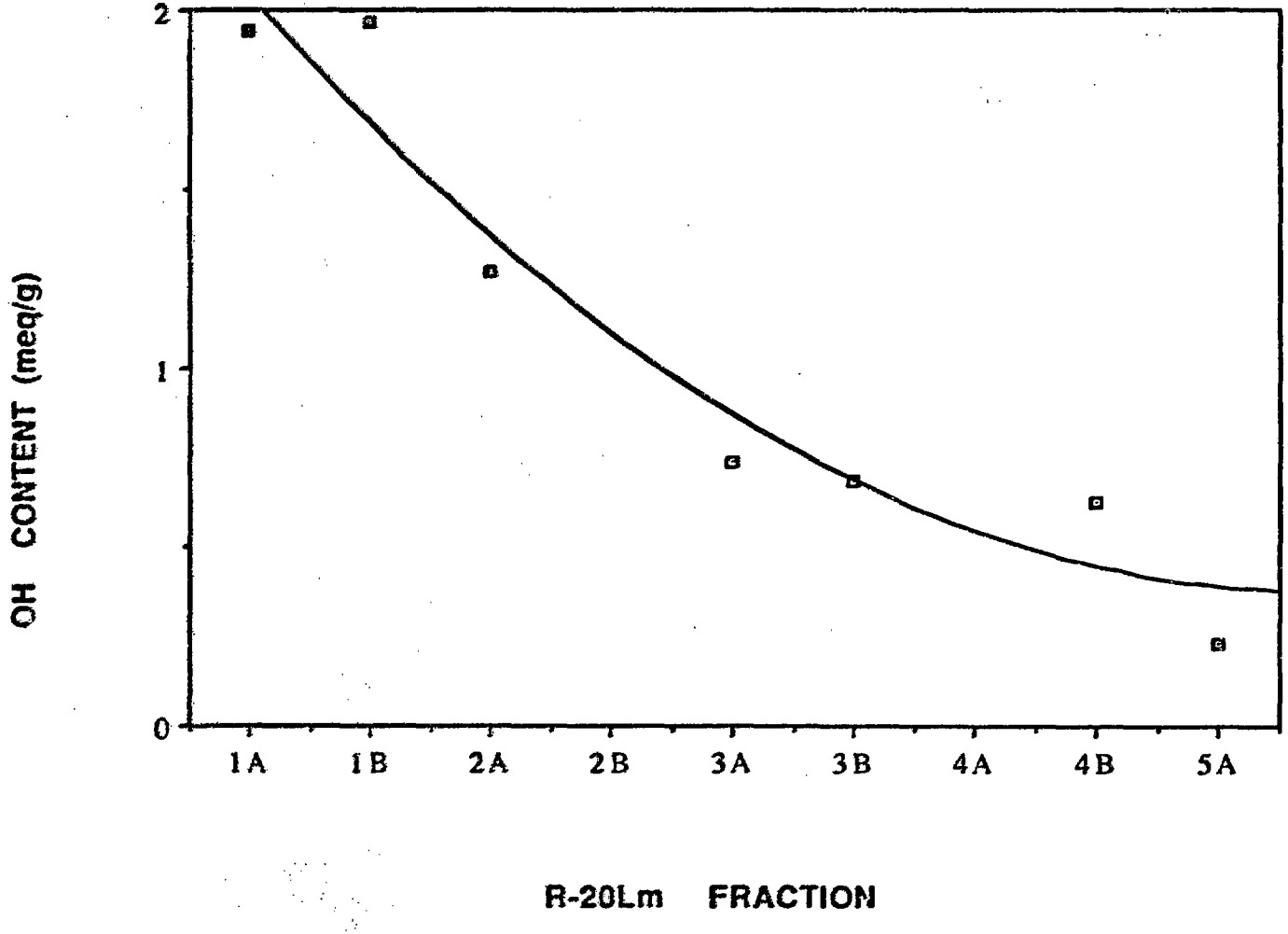

FIGURE 34. Plot of the hydroxyl data for Sartomer R20LM fractions reported in Table 88.

TABLE 89. Hydroxyl-Content Independence of Retentions of Molecular-Weight Probe Solutes

Solute	t/°C	V_g^o/cm^3 g^{-1} Lot 40	Lot ACH V004	Lot 42B
Butyronitrile	50	232.6	235.8	236.5
	60	160.5	162.0	163.2
	70	113.2	113.8	115.1
Valeronitrile	50	603.7	612.4	611.7
	60	397.3	400.1	403.1
	70	267.9	267.9	272.2
Prepolymer				
[OH]/meq g^{-1}		0.72	0.96	1.19
Mn/Da				

Table 90. Retentions of Molecular-Weight Probe Solutes with ARCO X Series of R-45M Standards

Solute	t/°C	V_g^o/cm^3 g^{-1} X-10LM	X-20LM	X-25LM	X-120HM	r[a]
Butyronitrile	50	306.7	287.6	276.7	249.4	0.999_9
	60	209.5	197.4	189.7	168.2	0.998_2
	70	146.3	138.5	133.0	116.1	0.994_0
Valeronitrile	50	780.0	733.8	706.6	642.4	0.999_9
	60	506.5	481.4	462.5	412.1	0.996_2
	70	337.3	323.6	310.3	271.3	0.986_8
Prepolymer						
[OH]/meq g^{-1}		1.73	1.40	1.18	0.59	
Mn/Da		1040	1350	1630	3335	

[a] Least-squares correlation coefficient of regression of V_g^o against Mn^{-1}.

Hydroxyl-Content Dependence of Retentions of Hydroxyl-Content Probe Solutes. A review of the solute retentions with the R-45M batches provided in Tables 60-65, Lots 40, ACH V004, and 42B, reveals two compounds that appear to reflect hydroxyl content, namely, acetone and chloroform at 30°C. The relevant data are provided below in Table 91. The retentions of acetone increase significantly on passing from Lot 40 (OH content of 0.72 meq g^{-1}) to 42B (OH of 1.19 meq g^{-1}); while those of chloroform increase less so.

[It is significant that the largest changes in the solute retentions occur at the lowest temperature evaluated. The presumed hydrogen-bonding interactions are undoubtedly weak to begin with because of the relatively low hydroxyl content of the prepolymers. As a result, the effects are evident only at the lowest temperature, and disappear when the system temperature is raised by as little as 10°. Therefore, to enhance retention differences from one lot of R-45M to another, either the temperature must be lowered still further, or another set of solutes chosen that interact more strongly with stationary-phase hydroxyls, e.g., small-molecule alcohols (methanol, ethanol, etc.). An evaluation of alcohol solutes was therefore undertaken; the results are provided in a later Section.]

A further test of the extent to which acetone and chloroform reflect hydroxyl content is given in Table 92, which provides the retentions with the X series of ARCO R-45M standards. The specific retention volumes decrease because the molecular weights of the prepolymers increase on passing from X-10LM through X-120HM. Thus, molecular-weight changes mask any effects due to hydroxyl content, as indicated earlier might well be the case. Retentions relative to those of the molecular-weight nitrile probe solutes must therefore be used, as was the case in what follows.

The acetone and chloroform retention data at 30°C relative to those of butyronitrile and valeronitrile solutes at 50-70°C are provided below in Table 93. There is a pronounced rise in all of the data on passing from X-10LM through X-120HM, i.e., with increasing hydroxyl content. The most notable change in the alpha values, that is, the solute most sensitive to hydroxyl content, is chloroform, relative to butyronitrile, at 50°C.

TABLE 91. Hydroxyl-Content Dependence of Retentions of Hydroxyl-Content Probe Solutes: Sartomer R-45M at 30°C

	$V_g^o/cm^3\ g^{-1}$		
Solute	Lot 40	Lot ACH V004	Lot 42B
Acetone	92.83	94.38	96.49
Chloroform	341.1	343.6	348.9
Prepolymer			
[OH]/meq g^{-1}	0.72	0.96	1.19
Mn/Da			

Table 92. Hydroxyl-Content Dependence of Retentions of Hydroxyl-Content Probe Solutes: ARCO R-45M at 30°C

	$V_g^o/cm^3\ g^{-1}$			
Solute	X-10LM	X-20LM	X-25LM	X-120HM
Acetone	115.9	111.4	107.7	100.4
Chloroform	382.3	368.9	361.0	353.3
Prepolymer				
[OH]/meq g^{-1}	1.73	1.40	1.18	0.59
Mn/Da	1040	1350	1630	3335

Table 93. Hydroxyl-Content Dependence of Relative Retentions of Hydroxyl-Content Probe Solutes: ARCO R-45M at 30°C

	Ref.	α			
Solute	t/°C	X-10LM	X-20LM	X-25LM	X-120HM
A. Butyronitrile Reference Solute					
Acetone	50	0.3779	0.3873	0.3892	0.4026
	60	0.5532	0.5643	0.5677	0.5969
	70	0.7922	0.8043	0.8098	0.8648
Chloroform	50	1.247	1.283	1.305	1.417
	60	1.825	1.869	1.903	2.101
	70	2.613	2.664	2.714	3.043
B. Valeronitrile Reference Solute					
Acetone	50	0.1486	0.1518	0.1524	0.1563
	60	0.2288	0.2314	0.2329	0.2436
	70	0.3436	0.3443	0.3471	0.3701
Chloroform	50	0.4901	0.5027	0.5109	0.5500
	60	0.7548	0.7663	0.7805	0.8573
	70	1.133	1.140	1.163	1.302
Prepolymer					
[OH]/meq g^{-1}		1.73	1.40	1.18	0.59
Mn/Da		1040	1350	1630	3335

Molecular-Weight-Independent Retention Indices. The method of determining hydroxyl content via relative retentions, as illustrated by the data provided in Table 93, has the drawback that capacity factors (at least) must be determined precisely and accurately at two temperatures. Moreover, the data are extremely temperature-dependent. It would therefore be useful if the method could somehow be modified so as to be relatively insensitive to changes in the column temperature, the flow rate, and so forth. One method of doing so is to use Kovats retention indices, I, as described below.

Retention indices are defined in most cases in terms of n-alkane marker solutes. However, it is clear from the data presented in this work that the retentions of such compounds are functions both of molecular weight and hydroxyl content and so, are unsuitable for the purpose of calculating relative retentions. However, Laub pointed out some time ago (17) that virtually any homologous series of compounds can be used to define retention indices, since the retentions of compounds differing by a discrete unit (a benzene ring, a methylene unit, etc.) will invariably regress linearly with "carbon number" (however this is defined).

Accordingly, the specific retention volumes for acetonitrile and propionitrile at 50-70°C, calculated from regressions of log V_g^o against carbon number for butyronitrile and valeronitrile, are given in Table 94. These data were then used to calculate retention indices relative to n-alkyl nitriles, here given the symbol I^{CN}, for acetone and chloroform solutes at 30°C. The results are shown in Table 95.

The data confirm, first, that the retention indices of the hydroxyl-content probe solutes reflect the increasing hydroxyl content of the stationary phases independent of molecular weight. Secondly, the retention-index changes are not trivial, particularly for chloroform solute at 50°C, which passes from 424 to 438. (Retention-index data generally are reproducible to ± 1 R.I. unit.) However, there remains considerable temperature variation of the data. For example, chloroform with X-10LM changes from 423 at 50°C to 515 at 70°C. Thus, the GC oven temperature control must be quite good if chloroform is used to assess hydroxyl content in this manner.

In order to alleviate the temperature dependence of the retention-index method, hydroxyl-content probe solutes need to be identified whose retentions are suitable at the same temperature(s) as is(are) used for the molecular-weight markers, that is, 50-70°C. However, the strength of hydrogen-bonding interaction would have to be greater than that of chloroform in order to be observable at the higher temperatures. Small-molecule alcohol solutes would seem to be useful in this regard; their suitability as hydroxyl-content probe solutes is assessed below. In the meantime, it is fair to say that solutes had been identified at this point whose retentions do in fact reflect the hydroxyl content of R-45M prepolymers; and that a method had been developed for taking into account variations in the molecular weight of the stationary phase.

Phase II, Task 3. Hydroxyl Distribution

Inverse GC work carried out to date has failed to identify probe solutes whose retentions can be linked unambiguously to hydroxyl distribution. For example, those of acetylacetone (2,4-pentadedione) with Lots 40, ACH V004, and 42B at 30°C are 1761, 1780, and 1754 $cm^3\ g^{-1}$, respectively; while the retentions of methyl butyl ketone are 1878, 1905, and 1876 $cm^3\ g^{-1}$. In fact, all of the monoketone solutes give a maximum with ACH V004. Thus, no distinction could be drawn between the retention patterns of the monoketone and diketone solutes. The matter thus invites further and comprehensive study in future efforts.

Table 94. Retentions of Acetonitrile and Propionitrile[a] with ARCO X Series of R-45M Standards at 50-70°C

t/°C	Solute	V_g^o/cm^3 g^{-1} X-10LM	X-20LM	X-25LM	X-120HM
50	Acetonitrile	47.42	44.18	42.43	37.59
	Propionitrile	120.6	112.7	108.4	96.83
	Butyronitrile	306.7	287.6	276.7	249.4
	Valeronitrile	780.0	733.8	706.6	642.4
60	Acetonitrile	35.84	33.19	31.91	28.02
	Propionitrile	86.65	80.95	77.81	68.65
	Butyronitrile	209.5	197.4	189.7	168.2
	Valeronitrile	506.5	481.4	462.5	412.1
70	Acetonitrile	27.52	25.37	24.43	21.26
	Propionitrile	63.46	59.28	57.01	49.68
	Butyronitrile	146.3	138.5	133.0	116.1
	Valeronitrile	337.3	323.6	310.3	271.3

[a] Derived from regressions of log V_g^o against carbon number.

Table 95. Retention Indices, I^{CN}, for Hydroxyl-Content Probe Solutes with ARCO X Series of R-45M Standards at 30°C

Solute	Ref. t/°C	I^{CN} X-10LM	X-20LM	X-25LM	X-120HM
Acetone	50	295.8	298.7	299.4	303.8
	60	332.9	335.8	336.5	342.4
	70	372.1	374.3	375.1	382.9
Chloroform	50	423.6	426.6	428.4	436.8
	60	468.1	470.1	472.2	482.8
	70	515.0	515.4	517.9	531.1

Phase III, Task 1. Inverse GC of Selected Lots of R-45M

The final Phase of the Contract was devoted to demonstrating the utility of IGC for the characterization of several lots of R-45M. In doing so, only conventional equipment was employed. For example, instead of the usual laboratory-constructed high-precision instrument that had heretofore been used to measure specific retention volumes, activity coefficients, etc., a Varian Model 14 commercial packed-column gas chromatograph was employed. Also, the columns were 5 ft by 1/8-in (ca. 3 mm), which were packed in the usual way with conventional supports (Chromosorb G: AW, DMCS-treated). Thus, all equipment, materials, and supplies used in what follows are readily available in any chemistry laboratory. The methods and techniques that are described could therefore be easily implemented.

Reproducibility of Capacity Factor Data. In order to assess in practical terms the usefulness of the inverse GC technique for the characterization of R-45M without extensive data acquisition/reduction necessary for specific retention volumes, it was first necessary to determine to what extent solute capacity factors, $k' [= (t_R - t_A)/t_A$, i.e., data taken directly from stripchart recordings] could be reproduced from column to column. If the k' could not be reproduced, then differences in lots of R-45M could not be detected. On the other hand, if the k' could be reproduced to within some reasonable error limit, then changes in the solute retentions could be ascribed to changes between lots of R-45M, rather than due just to instrumental artifact.

As a result, three separate columns containing 5% w/w X-120HM R-45M were run at this point with acetone, ethanol, propionitrile, propanol, chloroform, butyronitrile, and valeronitrile solutes at 80°C. The nitrile solutes were chosen because their retentions reflect changes in the stationary-phase molecular weight independently of hydroxyl content; while the remaining compounds, particularly the alcohols, reflect the OH content. Also, the temperature of 80°C was used because most commercial GC's cannot maintain column temperatures less than about 75°C with any accuracy. In addition, the flow rate was adjusted with each column to ca. 20 cm^3 min^{-1}; the retention of methane (presumed not to be retained with this system) was 0.60 min in each case. The results of the replicate runs are shown below in Table 96.

Table 96. Replicate Capacity Factors, k', of Indicated Solutes with X-120HM R-45M Stationary Phase at 80°C

		k'		
No.	Solute	Trial 1	Trial 2	Trial 3
1	Acetone	1.70	1.77	1.72
2	Ethanol	1.70	1.77	1.72
3	Propionitrile	3.50	3.53	3.53
4	Propanol	3.50	3.53	3.53
5	Chloroform	4.92	5.00	4.97
6	Butyronitrile	6.72	6.75	6.73
7	Valeronitrile	15.2	15.3	15.5

The data show, first, that the capacity factors are reproducible to at worst ± 2%, and then only for the most volatile solutes, acetone and ethanol (overlapped). Also, the retentions were measured simply with a stopwatch (the use of a modern integrator would therefore presumably improve the precision of measurement of the elution times). In any

event, it is clear from the results that the absolute capacity factor data with columns and conditions even with analytical GC's as simple as a Varian Model 14 are quite reproducible, and that the latter instrumentation is therefore suitable for the IGC of R-45M.

Variation of Retentions with R-45M. Table 97 presents the capacity factors of the solutes of Table 96 with the four ARCO standards, X-10LM, X-20LM, X-25LM, and X-120HM (the latter averaged over three trials); as well as with Sartomer R-20LM and Lots 40, 42B, and V004 of R-45M. The retentions as well as elution order change considerably on passing across the table for any given solute. For example, n-propanol and chloroform are well separation with X-10LM, overlap completely with X-20LM, are well separated again with X-25LM and X-120HM but with inversion of retention order, which reverses again with R20LM.

Table 97. Capacity Factors, k', of Solutes of Table 96 with Indicated Lots of R-45M Stationary Phase at 80°C

		k'							
No.	Solute	10LM	20LM	25LM	120HM	R20LM	40	42B	V004
1	Acetone	2.50	2.17	1.80	1.73	2.33	1.33	1.68	2.00
2	Ethanol	3.28	2.68	1.80	1.73	3.12	1.33	1.68	2.00
3	Propionitrile	5.17	4.43	3.37	3.52	4.68	2.72	3.22	3.80
4	Propanol	7.27	5.88	3.63	3.52	6.90	2.95	3.62	4.12
5	Chloroform	6.33	5.88	5.00	4.96	5.93	4.07	4.83	5.48
6	Butyronitrile	10.5	8.83	6.77	6.73	9.60	5.53	6.67	7.58
7	Valeronitrile	23.9	20.3	15.5	15.3	21.9	12.9	15.1	17.2

Variations in the retentions and retention order are visualized more easily by direct inspection of the chromatograms, which are shown below in Figures 35-40. The first four were obtained with X-10LM, X-20LM, X-25LM, and X-120HM R-45M stationary phases; while the latter two were with R20LM and lot 40.

The first chromatogram, Figure 35, shows solute no. 4, n-propanol, eluting well after no. 5, chloroform.

In Figure 36, obtained with X-20LM, nos. 4 and 5 overlap completely. No. 4 elutes well before no. 5 with X-25LM, Figure 37; however, it also overlaps considerably with no. 3, propionitrile. In addition, solutes 1 and 2, acetone and ethanol, are completely unresolved.

The solute pairs 1 with 2 and 3 with 4 are overlapped fully with X-125HM phase, Figure 38.

All solutes are well resolved with R20LM solvent, Figure 39, but the retention times (hence, capacity factors) are nearly as long as those found with X-10LM.

Finally, the retentions with lot 40 R-45M, Figure 40, result in solutes 1 and 2 being fully overlapped, 3 and 4 partially so, and 5, 6, and 7 being well separated, all with quite low retention times compared with any other lot of R-45M considered in this portion of the work.

The above results demonstrate that the IGC technique is indeed capable of distinguishing between lots of R-45M. Also, as detailed in previous Sections, nomographic reduction of the retentions yields in addition the stationary phase molecular weight and hydroxyl content. It is worth emphasizing at this point that the above work was carried out with a simple packed-column GC and stripchart recorder.

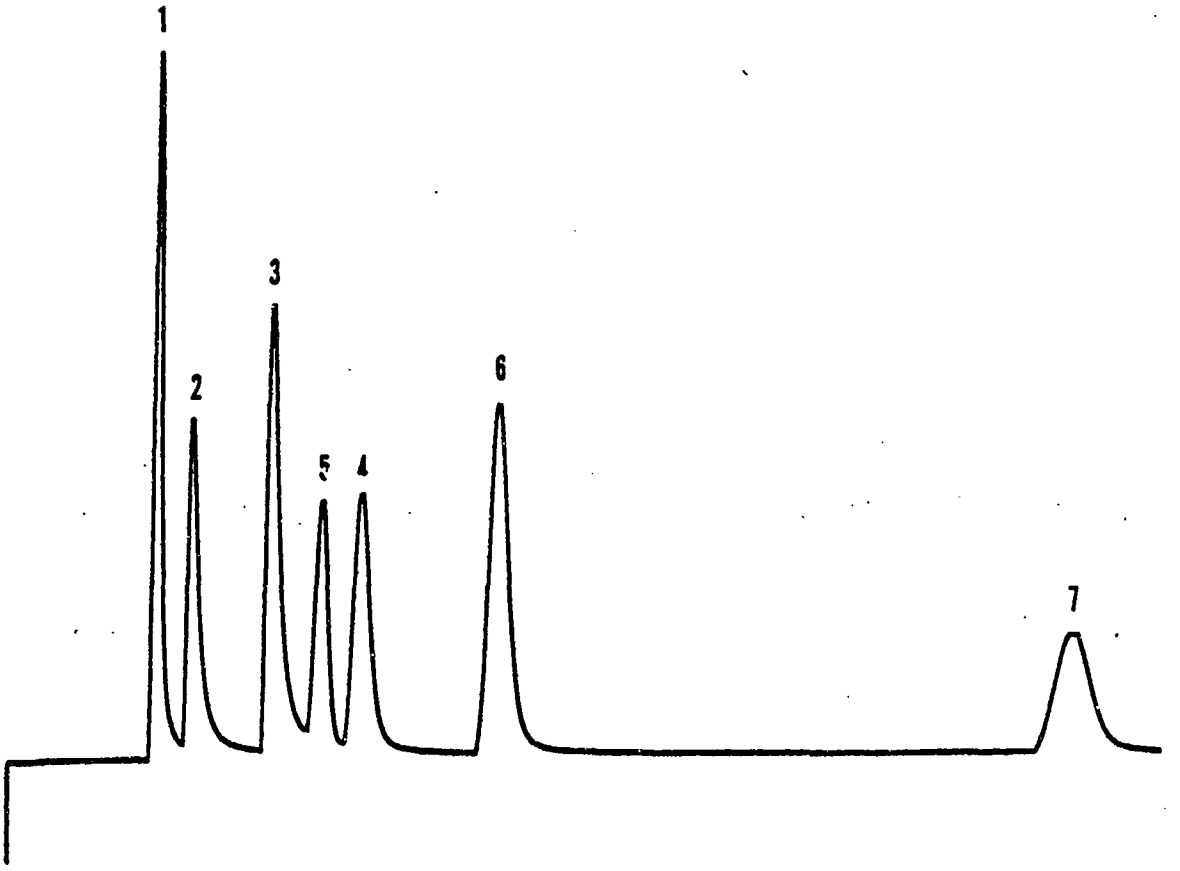

FIGURE 35. Packed-column gas chromatogram of solutes of Table 96 with X-10LM stationary phase at 80°C. See Text for column details and conditions.

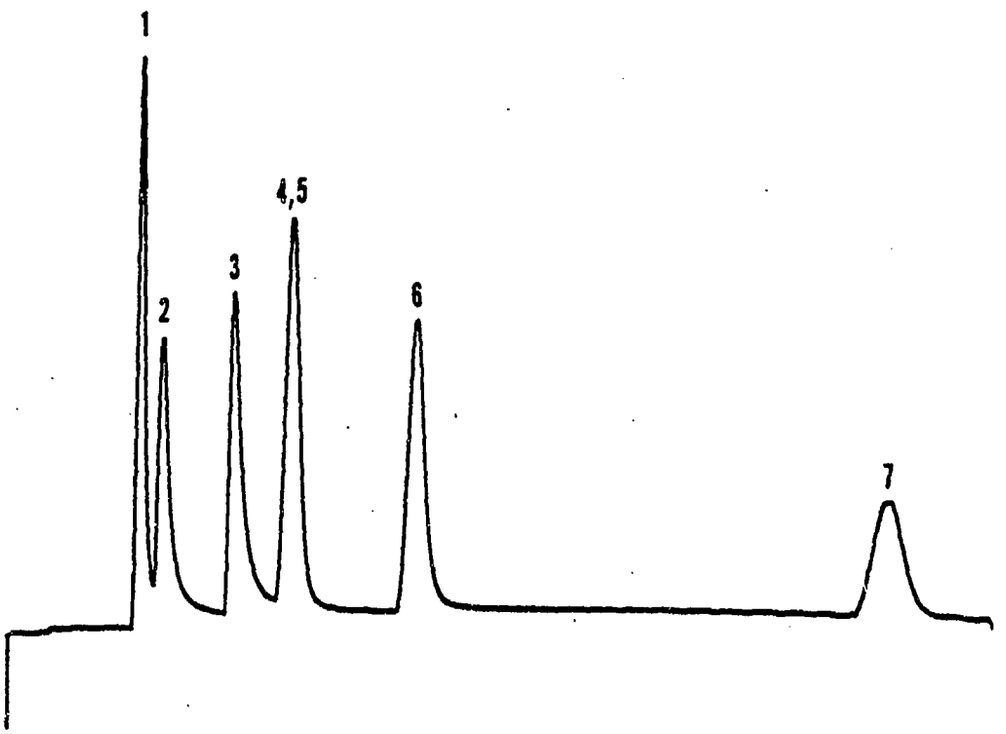

FIGURE 36. As in Figure 35; X-20LM stationary phase.

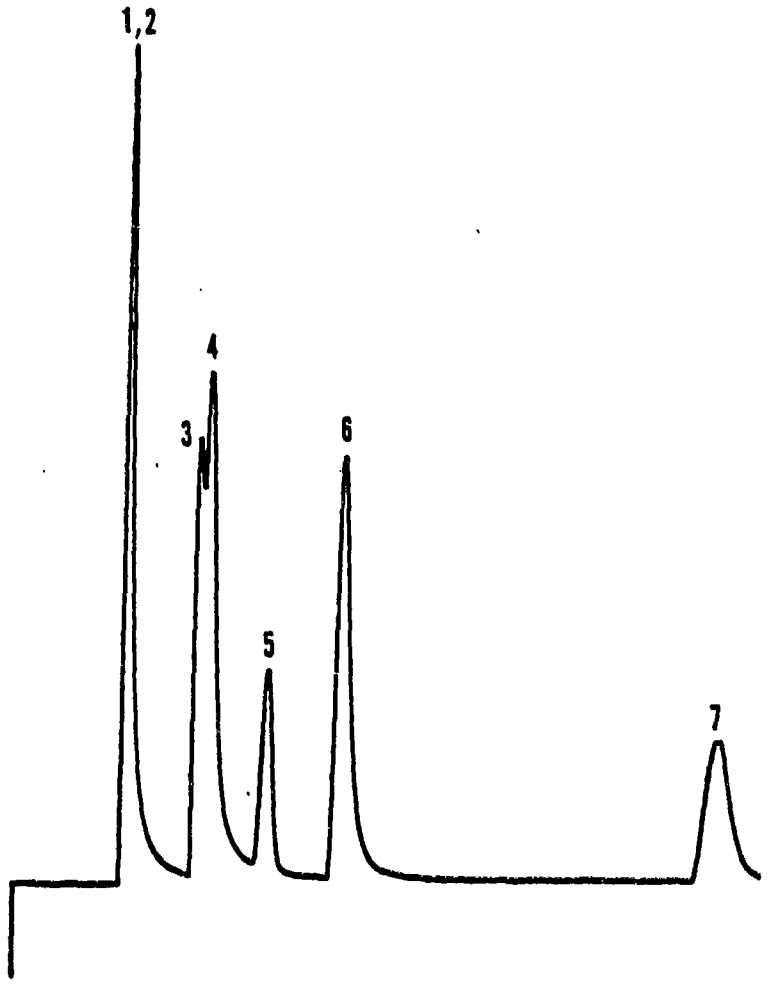

FIGURE 37. As in Figure 35; X-25LM stationary phase.

FIGURE 38. As in Figure 35; X-120HM stationary phase.

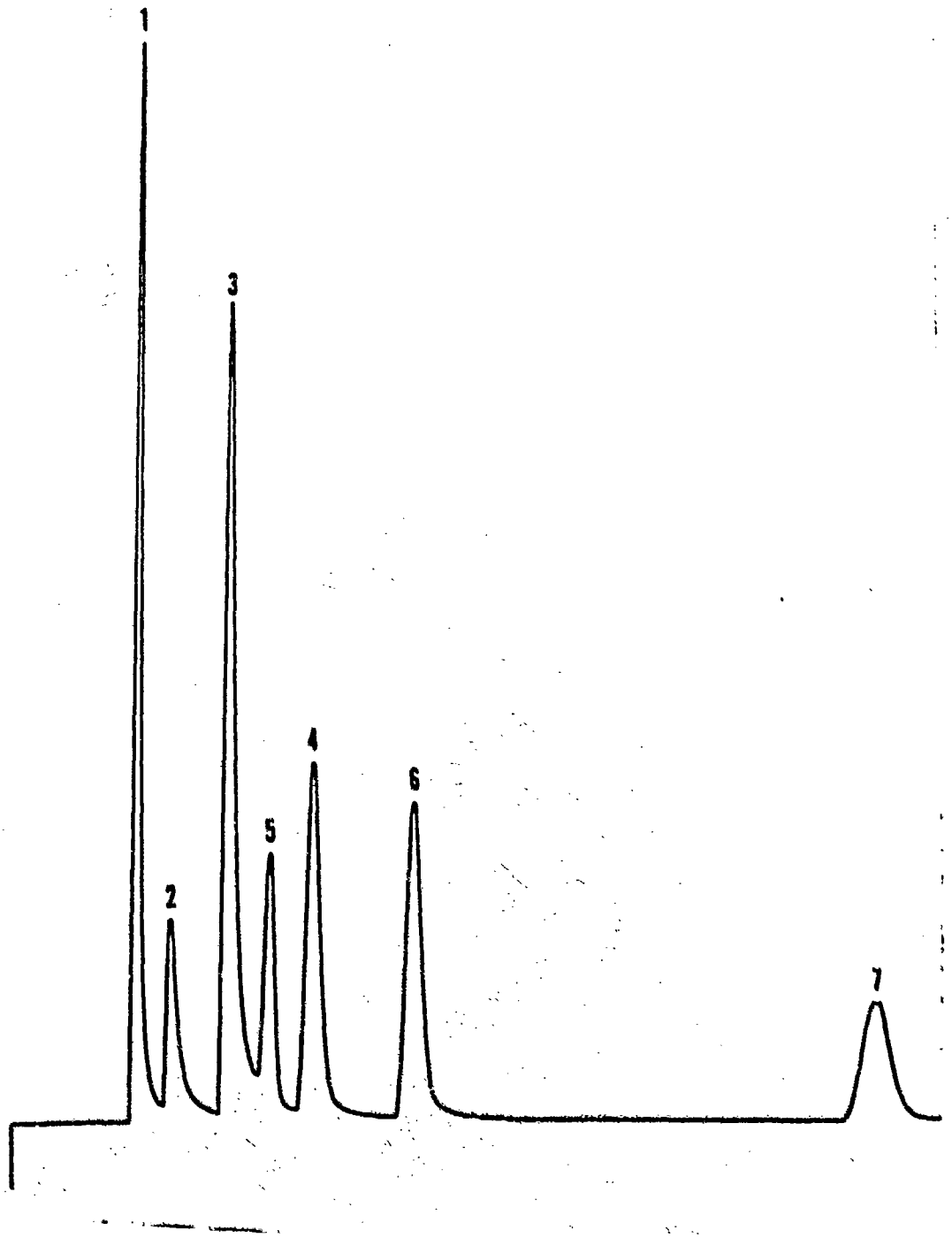

FIGURE 39. As in Figure 35; R20LM stationary phase.

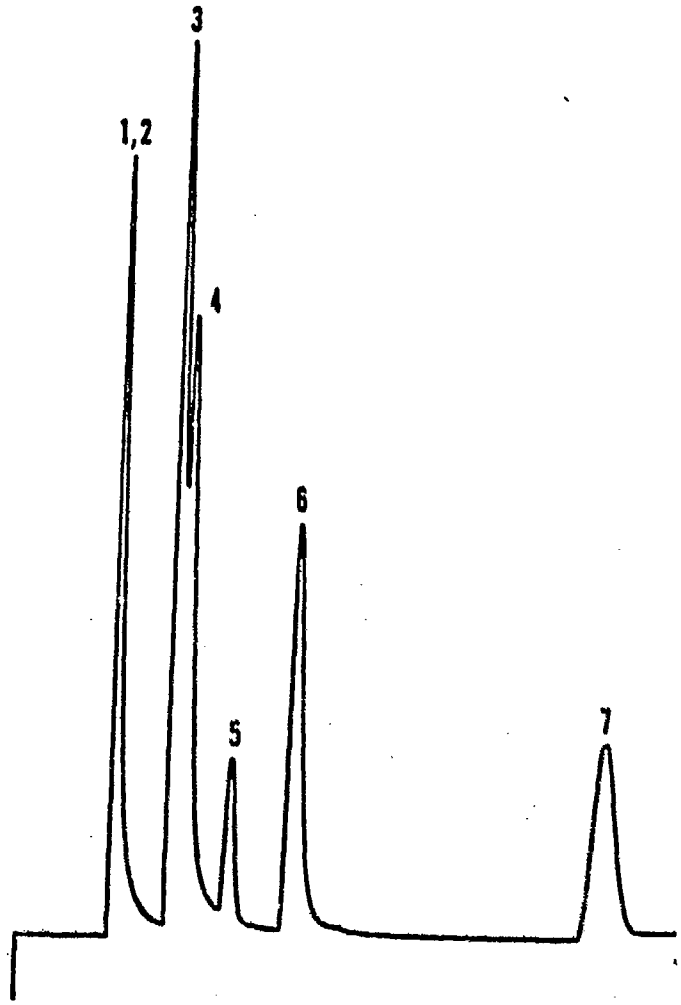

FIGURE 40. As in Figure 35; lot 40 stationary phase.

Phase III, Task 2. Chain Branching

Throughout the Contract, the (potential) effects of chain branching on the IGC retentions, the fractionation patterns, and so forth, were looked for. However, none were seen, as mentioned earlier. For example, the probe-solute GC retentions with the ARCO standard stationary phases correlated as expected: retentions were a linear function of the inverse molecular weight of the solvent. Also, once having taken molecular weight effects into account, the hydroxyl probe-solute retentions correlated directly with the hydroxyl contents of the stationary phase. Thus, no anomalous effects were detected. That is of course not to say that there is no chain branching in R-45M; rather, that chain branching could not be detected by the methods used. Even so, there is some evidence that GC retentions respond to chain branching (22). It may therefore prove possible to quantitate chain branching in polymers such as R-45M by some or other form of inverse chromatography, e.g., supercritical fluid chromatography.

SUMMARY AND CONCLUSIONS

The technique known as "inverse" gas chromatography (IGC) has been developed as a tool for the characterization of materials such as R-45M. The resultant practical methodologies and techniques make use only of simple commercially-available equipment, and can be applied to analysis and routine quality control of other prepolymer systems, particularly those that are not easily characterized by conventional means.

In the first part of the work, a new procedure for determining the number-average molecular weight of hydroxy-terminated polybutadiene by IGC was developed. The molar specific retention volumes, $V_g^o'/cm^3\ mol^{-1}$, of probe-solutes with well-characterized batches of R-45M were measured initially in order to identify compounds whose elution behavior correlated with M_n. (In this mode of data reduction the retentions should regress directly with molecular weight.) In the present instance, the retentions of chloroform at 30°C and valeronitrile at 30° and 50°C were found to provide significant distinction even between R-45M of 1350 and 1420 Da, independent of the prepolymer hydroxyl content; in contrast, alkane solutes were surprisingly poor indicators of M_n. Regression of the conventional-form specific retention volumes of the promising probe-solutes, $V_g/cm^3\ g^{-1}$, were used next to generate nomographs of inverse molecular weight, the linear least-squares correlation coefficients of which were in excess of 0.9999. The graphs were then employed to assess the M_n of other bulk and fractionated R-45M. (Parenthetically, the solvent fractionation patterns obtained with iso-propyl alcohol/benzene with the Sartomer sample of R-45M were quite different from the ARCO materials. Also, the gas-chromatographic specific retention volumes of the probe-solutes with the Sartomer lot of R-45M at 30-80°C were notably divergent from those observed with ARCO lots.) The retentions of several alkyl nitriles were thereby shown to correlate well with molecular weight, and were also demonstrated to be independent of the stationary-phase hydroxyl content.

The hydroxyl contents of all R-45M lots were next determined via FT-IR with nomographic Beer's law data using the standard 6-undecanol. The correlation coefficient of the nomograph was at least 0.999. However, a finite intercept limited the method to hydroxyl values of no less than ca. 20 meq dm^{-3}. The ARCO standards comprised of the "X" series, 10LM, 14LM, 20LM, 25LM, and 120HM, gave hydroxyl values that were in reasonable agreement with published data. The hydroxyl contents of the Sartomer R20LM fractions as well as those of all other bulk R-45M samples obtained from AL were compared with the inverse GC retentions. Acetone and chloroform solutes at 30°C were found to correlate linearly and positively with hydroxyl content (increasing retentions with increasing OH), while o- and p-xylene correlated linearly and negatively. Both the relative retentions and retention indices of acetone and chloroform (the latter based

upon the retentions of the nitrile standards at 50°C) were found to reflect quite accurately the hydroxyl content of R-45M prepolymer stationary phases.

The determination of retentions at one temperature relative to those at another is somewhat inconvenient as well as imprecise. An alternative procedure was therefore developed that made use of nitrile and alcohol solutes with simple analytical gas chromatographic instrumentation and packed columns at 80°C. Chromatograms of the molecular-weight and hydroxyl marker compounds with ARCO, Sartomer, and AL batches of R-45M under these conditions did indeed exhibit quite dramatic shifts in the probe-solute retentions, in accordance with the respective M_n and OH contents of the stationary phases. The quantitation of R-45M prepolymer molecular weight and functionality by inverse gas chromatography, making use only of a simple set of probe-solutes and GC instrumentation and conditions, was thus brought to hand.

REFERENCES

1. Carver, J. G., Improved Specifications for Composite Propellant Binders for Army Weapon Systems, Technical Report T-79-76, U.S. Army Missile Command, Redstone Aresenal, Alabama, July 1979.

2. Carver, J. G., Rapid Method for Determination of Functionality Distribution in Hydroxy-Terminated Polymers, in Proceedings of the 1980 JANNAF Propellant Characterization Subcommittee Meeting, Publication 333, Chemical Propulsion Information Agency, Laurel, Maryland, October 1980.

3. Thompson, G., and Daly, E. E., Development of HTPB Propellant for Ballistic Missiles, Final Technical Report TWR-8618, Vol. II (AFRPL-TR-75-23, Vol. II), November 1974.

4. Law, R. D., An Evaluation of Derivatives of HTPB Used in the One-Step Determination of Average Functionality Profile, in Proceedings of the 1980 JANNAF Propellant Characterization Subcommittee Meeting, Publication 333, Chemical Propulsion Information Agency, Laurel, Maryland, October 1980.

5. Christian, T. W., Chemical Characterization of HTPB Prepolymers, Report No. LS79-29, Chemical Propulsion Information Agency, Laurel, Maryland, June 1979.

6. Brown, R. D., Literature Survey on Hydrocarbon Binders for Solid Rocket Propellants, Publication 251, Chemical Propulsion Information Agency, Laurel, Maryland.

7. Myers, G. E., Optimization of HTPB Binder, Final Technical Report LPC-436-F (AFRPL-TR-71-123), January 1972.

8. Grubisic, Z., Rempp, R., and Benoit, H., Journal of Polymer Science, Part B, Vol. 5, p. 753, 1967. See also: Cantow, M. J. R., and Johnson, J. F., Journal of Applied Polymer Science, Vol. 11, p. 1851, 1967; Journal of Polymer Science, Part A-1, Vol. 5, p. 2835, 1967.

9. Laub, R. J., and Pecsok, R. L., Physicochemical Applications of Gas Chromatography, Wiley-Interscience, New York, 1978.

10. Laub, R. J., Purnell, J. H., Williams, P. S., Harbison, M W. P., and Martire, D. E., Journal of Chromatography, Vol. 155, p. 233, 1978.

11. Laub, R. J., Prepolymer Characterization, Final Technical Report AFAL-TR-88-068, Air Force Astronautics Laboratory, Edwards Air Force Base, California, Octol.. 1988.

12. Hinney, H. R., Babiec, Jr., J. S., and Murphy, J. R., New Hydroxyl Terminated Polybutadiene Resins, in Proceedings of the 1984 JANNAF Propellant Characterization Subcommittee Meeting, Publication 413, Chemical Propulsion Information Agency, Laurel, Maryland, 1984, p. 147.

13. Arnold, M. T., Baghdadchi, J., Hinney, H. R., and Meyers, J. A., New Polymeric Binder Resins, in Proceedings of the 1985 JANNAF Propellant Characterization Subcommittee Meeting, Publication 435, Chemical Propulsion Information Agency, Laurel, Maryland, 1985, p. 245. The ARCO Division that manufactures R-45M has since been sold to Sartomer Co. (West Chester, PA), which has since been sold again to Elf Aquitaine. These standard lots are therefore no longer available.

14. Beilsteins Handbuck der Organischen Chemie, Vol. 17 (No. 1), Springer-Verlag, Berlin, 1974, p. 26.

15. Ambrose, D., and Townsend, R., Vapor-Liquid Critical Properties, National Physical Laboratory, Teddington, Middlesex, U.K., 1979.

16. Dreisbach, R. R., Physical Properties of Chemical Compounds, American Chemical Society, Washington, D.C., Vol. I (1955); Vol. II (1959); Vol. III (1961).

17. Laub, R. J. Analytical Chemistry, Vol. 52, p. 1219, 1980; Vol. 56, pp. 2110,2115, 1984.

18. Ambrose, D., Ellender, J. H., Lees, E. B., Sprake, C. H. S., and Townsend, R. Journal of Chemical Thermodynamics, Vol. 7, p. 453, 1975.

19. Nakanishi, K., and Toyama, O., Bulletin of the Chemical Society of Japan, Vol. 45, p. 3210, 1972.

20. Weast, R. C., Ed., Handbook of Chemistry and Physics, 67th ed., CRC Press, Cleveland, 1986.

21. Emanuel, L. J., and Dee, L. A., Semi-Micro Hydroxyl Equivalent Weight Methods, Technical Report AFRPL-TR-82-041, Air Force Astronautics Laboratory, Edwards Air Force Base, California, July 1982. See also: Emanuel, L. J., and Park, T. W., A Hydroxyl Equivalent Weight Interlaboratory Study, Technical Report AFRPL-TR-84-088, Air Force Astronautics Laboratory, Edwards Air Force Base, California, December 1984.

22. Littlewood, A. B., Analytical Chemistry, Vol. 36, p. 1441, 1964.